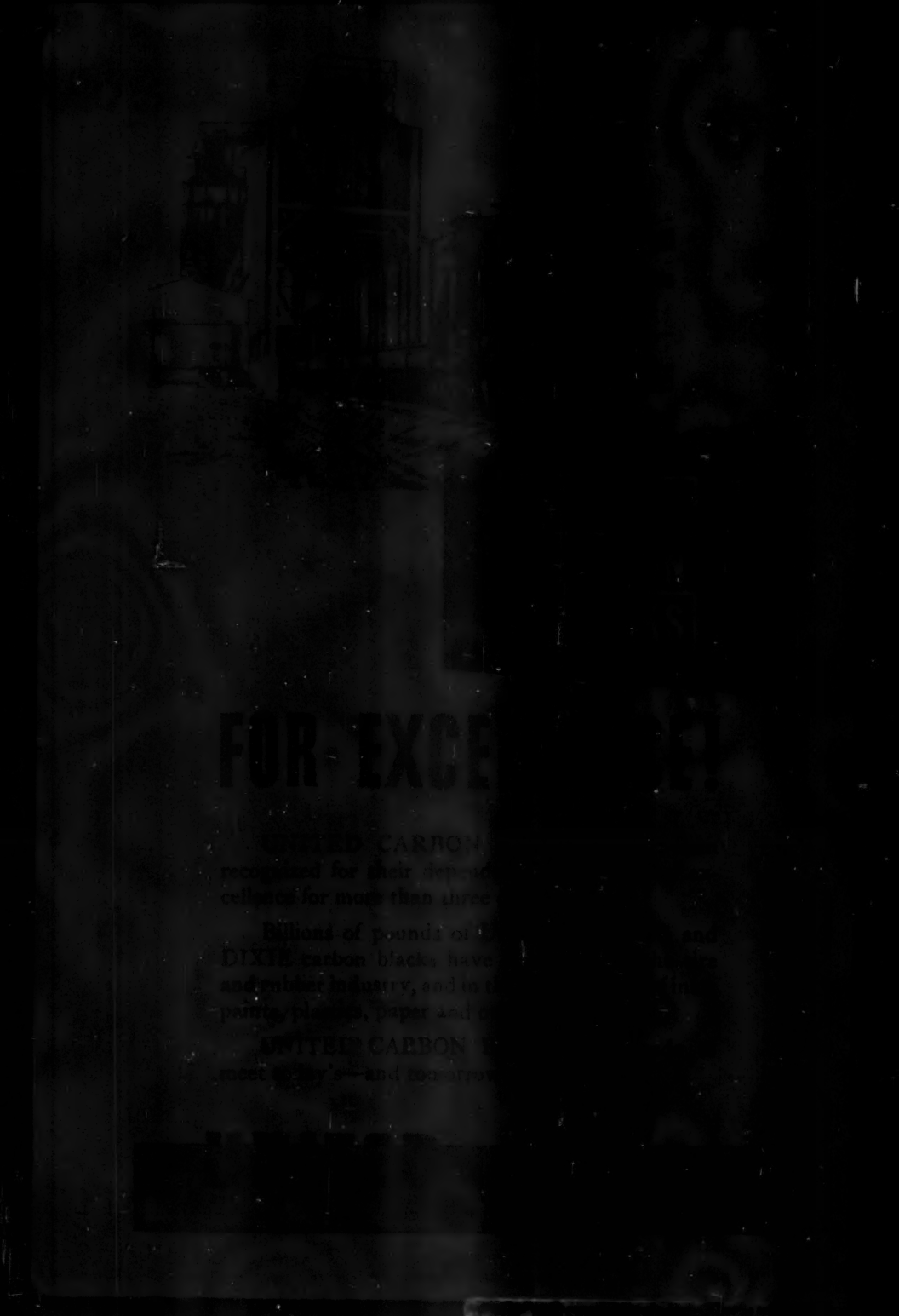

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Polysar Krylene
Polysar Krylene NS
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Polysar Krynol 651
Polysar Krynol 652
Polysar S-630

OIL RESISTANT

Polysar Krynac 800
Polysar Krynac 801
Polysar Krynac 802
Polysar Krynac 803

SPECIAL PURPOSE

Polysar SS-250
Polysar S-X371
Polysar Kryflex 200
Polysar Kryflex 252
Polysar SS-250 Flake

BUTYL

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Polysar Butyl 101
Polysar Butyl 200
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For help with specific recipes, call your Phillips technical representative. The resources of Phillips technical service laboratory are at your service!

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O — **Philblack O, High Abrasion Furnace Black.** For long, durable life. Good conductivity. Excellent flex life and hot tensile. Easy processing.

I — **Philblack I, Intermediate Super Abrasion Furnace Black.** Superior abrasion. More tread miles at moderate cost.

E — **Philblack E, Super Abrasion Furnace Black.** Toughest black yet! Extreme resistance to abrasion.

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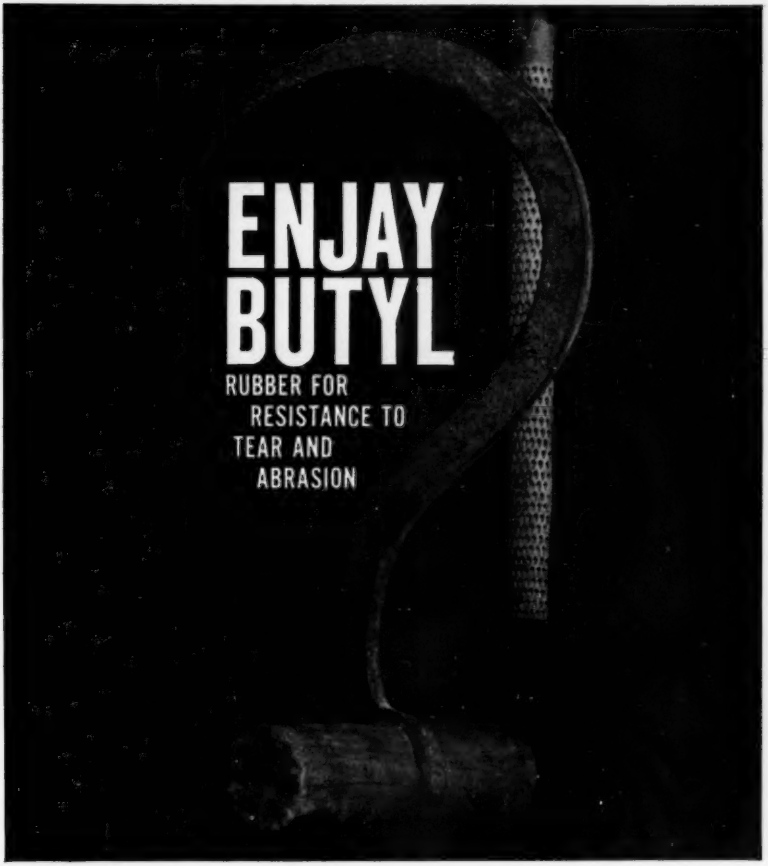

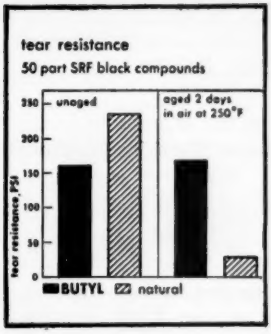

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Butyl also offers . . . outstanding resistance to chemicals, weathering, sunlight, heat, and electricity . . . superior damping qualities . . . unmatched electrical properties and impermeability to gases and moisture.

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Accelerator 808	Permalux	Thiuram M
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Conac S	Tepidone	Zenite
MBT	Tetrone A	Zenite Special
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Antox	Neozone D	Zalba Special
	Permalux	

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Rubber Red PBD	Rubber Green FD
Rubber Red 2BD	Rubber Blue PCD
Rubber Yellow GD	Rubber Blue GD
Rubber Green GSD	Rubber Orange OD

ORGANIC ISOCYANATES

Hylene* M	Hylene* T
Hylene* M-50	Hylene* TM
Hylene* MP	Hylene* TM-65

PEPTIZING AGENTS

Endor	RPA No. 3 Concentrated
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If you need a rubber reinforcing resin, Goodyear has the ideal answer in PLIOLITE S-6B. And when it comes to nitrile polymers, CHEMIGUM provides *extra* oil resistance and processability.

These outstanding products are backed by *personalized* service—a competent staff of experts stand ready to give you complete technical assistance *when you need it*. To take advantage of all the "extras" Goodyear offers – including free *Tech Book Bulletins*, just write to: Goodyear, Chemical Division, Dept. J-9430, Akron 16, Ohio.

GOODYEAR

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M-B-T
M-B-T-S
O-X-A-F
DELAC-S

Thiurams
Tuex®*
Ethyl Tuex*
Monex®*
Pentex
Pentex Flour

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Arazate®
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Ethazate 50-D
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C-P-B®
Z-B-X

Vulcanizing Agents
G-M-F
Dibenzo G-M-F

ACTIVATOR

D-B-A Accelerator

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Aranox®
B-L-E-25
Flexamine
V-G-B®

Nondiscoloring
Polygard®
Naugawhite
Naugawhite Powder

Semi-nondiscoloring
Octamine
Betanox Special®

Antiozonants
Flexzone 3-C
Flexzone 6-H

BLOWING AGENTS

Celogen® Celogen-80 Celogen-AZ®

SUNPROOFING WAXES

Sunproof® Regular Sunproof® Improved Sunproof® Jr.
Sunproof®-713 Sunproof® Super

MISCELLANEOUS SPECIAL PRODUCTS

BWH-1—mixture of oils

DDM—dodecyl mercaptan

LAUREX®—zinc laurate

PROCESS STIFFENER *710—26.4% hydrazine salt and 73.6% inert mineral filler

THIOSTOP K—50% aqueous solution of potassium dimethyl dithiocarbamate

THIOSTOP N—40% aqueous solution of sodium dimethyl dithiocarbamate

TONOX—p,p'-diaminodiphenylmethane

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RETARDER E-S-E-N RETARDER J

*available in Nauget form

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Division of United States Rubber Company Naugatuck, Connecticut

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CANADA: Naugatuck Chemicals Division, Dominion Rubber Co., Ltd., Elmira, Ontario · CABLE: Rubexport, N.Y.

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PARACRIL 18-80—Moderate oil resistance, excellent low-temperature flexibility.

PARACRIL AJ—Moderate oil resistance, easy processing, very good low-temperature performance.

PARACRIL ALT*—Low-temperature polymerized, high physicals, excellent low-temperature properties.

PARACRIL B—Good oil resistance, moderate low-temperature flexibility.

PARACRIL BJ—Like B but lower Mooney for easy processing.

PARACRIL BLT*—Low-temperature polymerized; high physicals, excellent processing.

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PARACRIL C—High oil resistance, fair low-temperature flexibility.

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*New Cold types

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FOR UNUSUALLY HIGH ABRASION RESISTANCE... USE HYCAR 1072

This carboxyl-modified nitrile rubber gives a compound far more abrasion resistance than any other rubber. During laboratory testing, garnet paper actually wears out without making any headway against this Hycar rubber.

Hycar 1072 gives all the advantages of isocyanate rubber at considerably lower cost, besides providing easier processing. In addition, Hycar 1072 will provide high gum strength, good hot tensile and tear strength, and good oil resistance combined with resistance to ozone.

Hycar 1072 offers new opportunities for makers of caster wheels, skate wheels, hard rolls, loom parts, football shoe calks and shoe heels.

For further information about Hycar 1072, or information about any of the many other Hycar nitrile rubbers or latices, write Dept. CD-2, B.F.Goodrich Chemical Company, 3135 Euclid Avenue, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

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Rubber and Latex

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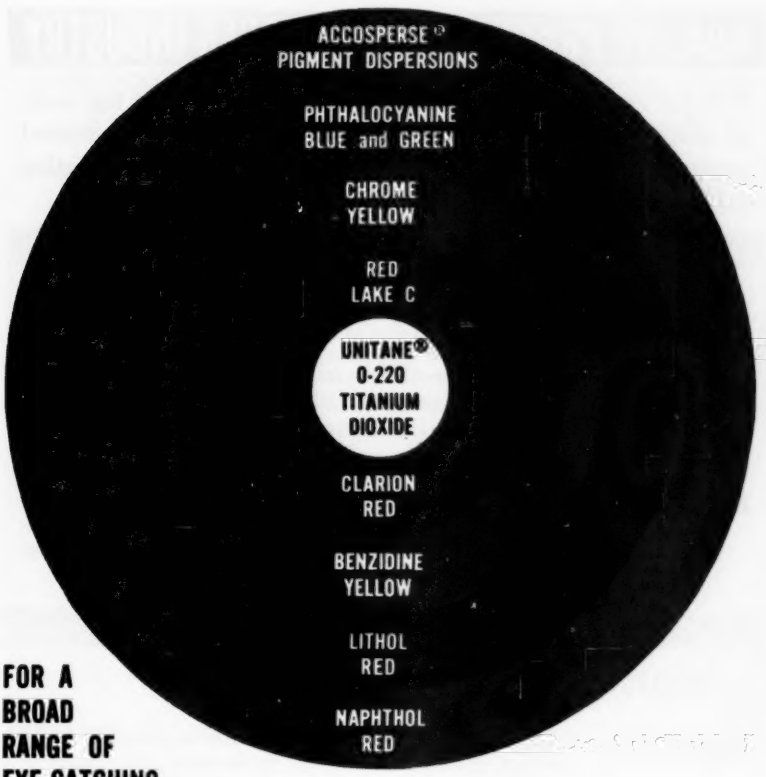
GEON vinyls • HYCAR rubber and latex • GOOD-RITE chemicals and plasticizers



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GEN-TAC • Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.

KO-BLEND • Latex-compounded masterbatch, 85% insoluble sulfur colloidally dispersed in SBR latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

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RUBBER

GENTRO • Top-quality cold SBR Polymers.

GENTRO-JET • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES

GEN-FLO • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

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VYGEN • a complete family of top-quality, versatile resins formulated to meet specific needs.

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Chemical Division GENERAL

Made by the originators of custom-blended Sunoco gasolines . . .

Sunoco's "Custom-Made" Process Oils Ease Problems of Quality Control

IF YOU PROCESS	USE	BECAUSE
Light-colored oil-extended polymers (1703, 1708, etc.)	CIRCOSOL® NS	It combines superior nonstaining characteristics with best processibility, imparts good physicals. Primarily an extender.
Oil-extended polymers (1703, 1708, etc.)	CIRCOSOL 2XH	It's a general-purpose softener and extender for light-colored rubber goods, especially where optimum physicals are required.
Regular neoprenes, natural rubber, SBR polymers, Hypalon (where color is a problem)	CIRCO® LIGHT	It's an ideal all-around moderate-priced plasticizer for nonstaining reclaims and butyl inner tubes, SBR, GN, W, WRT.
Oil-extended polymers (1705, 1710, etc.) and natural rubber, Hypalon (where color is no problem)	SUNDEX® 53	It's a double-distilled aromatic plasticizer for tire-tread stock, rubber footwear, matting, toys, semi-hard rubbers, high-Mooney WHV.
Black masterbatch polymers 1706, 1711, 1712, etc.	SUNDEX 1585	It's a new highly aromatic plasticizer for tough polymers where easy processing is desired. This is a distilled process aid.
Natural rubber, SBR polymers, regular and WHV neoprenes, acrylonitrile polymers	SUNDEX 85	It's especially recommended for very high loadings of WHV neoprene (from 75 to over 100 parts Sundex 85 to 100 parts polymer). Used in hard rubber goods.

Other Sun compounding oils, not listed, include a series of paraffin oil with low aromatic content; naphthenic oils with moderate aromatic content; and Sundex oils with high aromatic content. Sun's brochure: "A GRAPHIC METHOD FOR SELECTING OILS USED IN COMPOUNDING AND EXTENDING BUTADIENE-STYRENE RUBBERS" can help you select the best oil for your needs. Get a copy from your Sun man or write Dept. RC-10.

INDUSTRIAL PRODUCTS DEPARTMENT

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PHILADELPHIA 3, PA.

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Philprene* offers a tremendous variety!

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	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
HOT	PHILPRENE 1000 PHILPRENE 1001 PHILPRENE 1006 PHILPRENE 1009 PHILPRENE 1018 PHILPRENE 1019	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	PHILPRENE 1601 PHILPRENE 1603** PHILPRENE 1605 **Pigmented with EPC Black
COLD OIL	PHILPRENE 1703 PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 PHILPRENE 6608 PHILPRENE 1805 PHILPRENE 6620 PHILPRENE 6604 PHILPRENE 6661*** PHILPRENE 6682*** ***Carbon black slurry made by Philjet* Process

There are non-staining Philprene rubbers for white-wall tires, appliance door gaskets and window seals. Light colored Philprenes for surgical goods and shoe soles. Also Philprene rubbers with tremendous abrasion resistance and long flex life . . . special Philprene polymers for the wire and cable industry . . . for nearly *everything* that's made of rubber!

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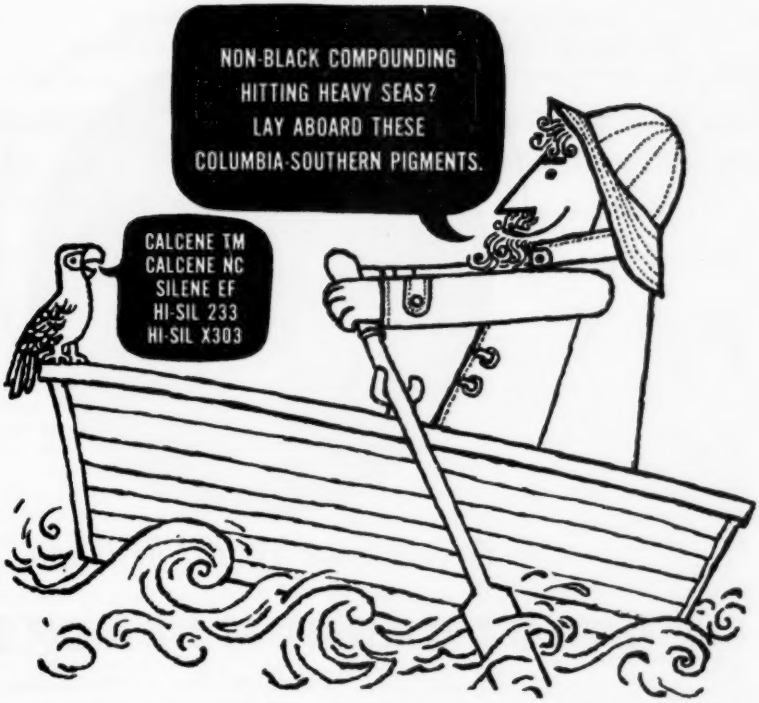

Don't let rugged compounding problems make you "abandon ship" . . . or steer you into just any old port-in-a-storm. Get complete information and comparisons on Columbia-Southern's family of white reinforcing pigments. As a group, these five pigments give an unexcelled range of physical properties to stocks of any desired shade or tone, including black. Superior compounds can be realized at refreshingly low costs.

CALCENE® TM—Coated, precipitated Calcium Carbonate for improved hot tear resistance, low modulus and higher tensile strength.

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SILENE® EF—Finely divided hydrated Calcium Silicate for greater abrasion, scuff or mar resistance, improved elongation, higher tensile strength.

HI-SIL® 233—Hydrated Silica offering outstanding tear and abrasion resistance, very high tensile strength, high modulus at a most competitive price.

HI-SIL® X303—Hydrated Silica designed with the high purity required by silicone rubber processors.

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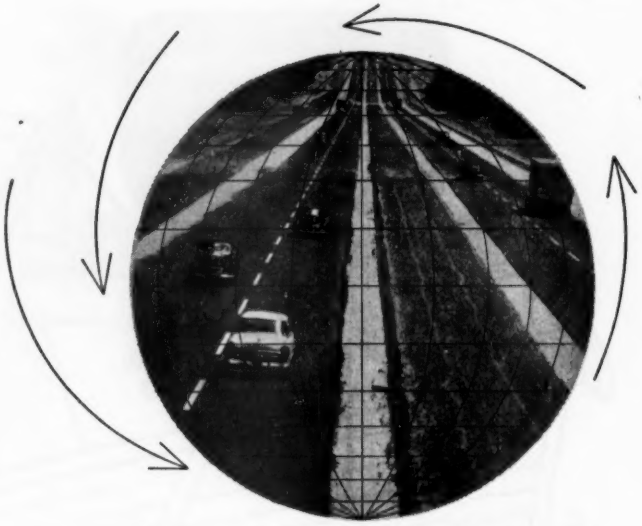

Around the World Mileage

with **CABOT CARBON BLACKS**

CHANNEL · FURNACE · THERMAL

For MAXIMUM RUBBER MILEAGE, whether in tires or in other rubber goods, Cabot offers the best quality, greatest variety of carbon blacks available. As the world's only manufacturer of a complete range of channel, furnace and thermal blacks, Cabot is able to offer a black to satisfy your every rubber requirement. That's why leading manufacturers of all types of rubber products continue to specify Cabot. For best carbon black performance, ask for . . .

CHANNEL BLACKS:	Spheron 9 EPC	Spheron 6 MPC		
FURNACE BLACKS:	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Vulcan XC-72 ECF
Vulcan SC SCF	Vulcan C CF	Sterling 99 FF	Sterling SO FEF	Sterling V GPF
Sterling L HMF	Sterling LL HMF	Sterling S SRF	Sterling NS SRF	Pelletex SRF
Pelletex NS SRF	Sterling R SRF	Gastex SRF		
THERMAL BLACKS:	Sterling FT	Sterling MT	Sterling MT-NS	
	Sterling FT-FF	Sterling MT-FF	Sterling MT-NS-FF	

Free Samples, Technical Literature Available

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125 HIGH STREET, BOSTON 10, MASSACHUSETTS

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MONSANTO RUBBER CHEMICALS ANSWER ANOTHER IMPORTANT COMPOUNDING QUESTION

QUESTION: *What economical vulcanizing agent can give my stocks highest heat resistance and more safety from scorch with no bloom or discoloration?*

ANSWER: *SULFASAN R dithioamine vulcanizing agent*

You can get the best heat resistance at a reasonable cost *and* eliminate bloom in your finished compounds by partial replacement of conventional curing agents with SULFASAN R. At the same time, this unique vulcanizing agent provides greater safety from scorch and can also boost modulus, lower compression set and improve aging.

Economical SULFASAN R trims the cost of some compounds by reducing the total amount of vulcanizing agent required. As little as 0.8 to 2 parts of SULFASAN R per hundred of rubber, plus a small amount of THIURAD (tetramethylthiuram disulfide) or a similar curing agent, is usually sufficient to achieve good results in GR-S, butyl, nitrile and natural rubbers. For more information, use the convenient coupon.

	HEAT RESISTANCE	
COMPOUNDS	**A**	**B**
Nitrile Rubber	100	100
Zinc Oxide	5	5
Stearic Acid	1	1
FEF Black	40	40
THIURAD	3.50	0.80
SULFASAN R	—	0.80
CURING AGENT COST	$3.99	$2.15
RESULTS		
Mooney Scorch (Mins.), Large Rotor @ 250° F.	12.5	31
Compression Set 70 Hrs./100° C.	27%	24%
Blooming	1 day	None in 9 months
Unaged		
Tensile, psi	2480	2520
Elongation, %	530	500
Hardness	64	65
Aged 70 Hrs./300° F.		
Tensile, psi	600	780
Elongation, %	20	30
Hardness	85	87

See how a lower-cost SULFASAN R/THIURAD system compares with THIURAD alone in a heat-resistant nitrile rubber compound.

LET MONSANTO RUBBER CHEMICALS ANSWER YOUR NEXT COMPOUNDING QUESTION

Jot it down on your letterhead. No obligation—no salesman will call (unless you so request). To help you solve specific problems, Monsanto draws from basic knowledge of more than 85 rubber chemicals and over 18,000 compounding studies. Write, today.

SULFASAN, THIURAD: Monsanto T. M.'s, Reg. U. S. Pat. Off.

Monsanto Chemical Company
Rubber Chemicals Department
Akron 11, Ohio

☐ Please send me more information about SULFASAN R

*Name*_____ *Title*_____

*Company*_____

*Address*_____

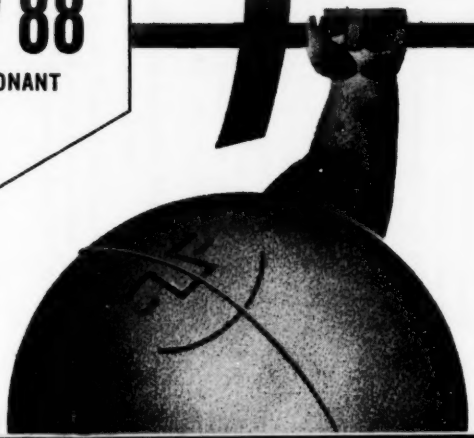
*City*_____ *Zone*____ *State*_____

Monsanto

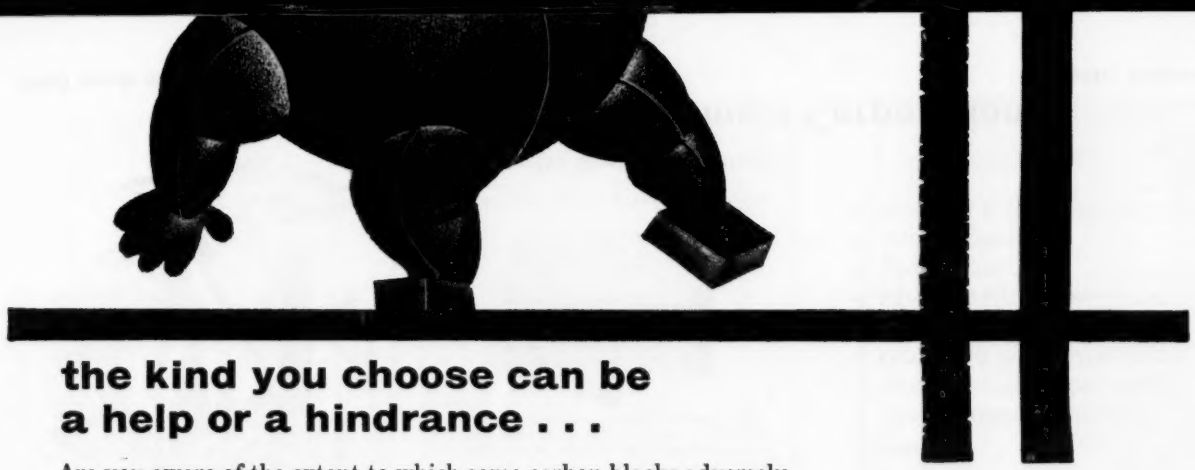
what type of CARBON BLACK helps fight ozone attack?

UOP 88®
ANTIOZONANT

UOP 288®
ANTIOZONANT



The SBR specimens below were exposed to ozone at 100° F, 20 percent elongation, 52 hr. at 33 pphm ozone, then 187 hr. at 63 pphm ozone.



the kind you choose can be a help or a hindrance . . .

Are you aware of the extent to which some carbon blacks adversely affect the protection afforded rubber products by antiozonants?

Some inactivate much of the antiozonant added for ozone protection. Others are more compatible with the antiozonant.

The two rubber test strips shown at right are clear evidence that carbon black plays an extremely important part in obtaining maximum service life of rubber compounded with antiozonants.

In formulating rubber compounds which must have high resistance to ozone, look to Universal for assistance. Special facilities and technical personnel are available to serve you. Write or telephone our Products Department.

(Left) Carbon black—EPC (easy processing channel), Curing system—2 phr sulfur, 2 phr benzothiazyl disulfide, Hours to first crack—31 to 47.

(Right) Carbon black—HAF (high abrasion furnace), Curing system—2 phr sulfur, 2 phr benzothiazyl disulfide, No cracks in 239 hr.

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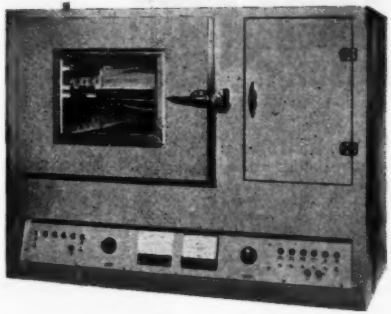

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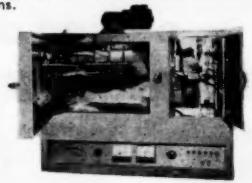

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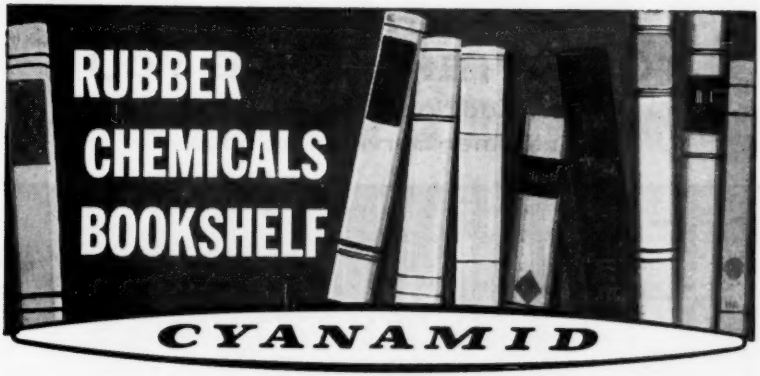

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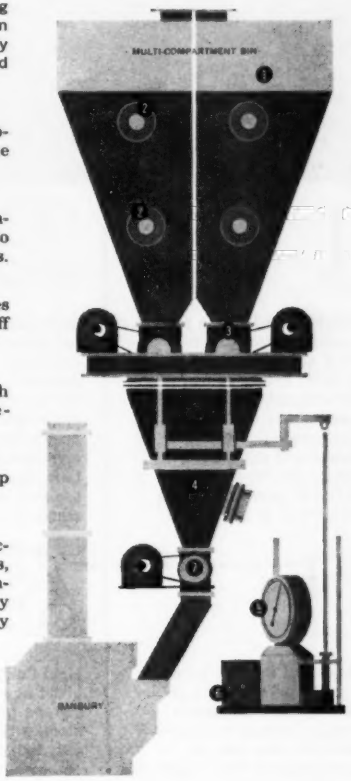

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Volume XXXII • Number Five

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Meeting		City	Hotel	Date
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1960	Fall	New York	Commodore	September 13–16
1961	Spring	Louisville	Brown	April 18–21
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	April 24–27
1962	Fall	Cleveland		October 16–19
1963	Spring	Toronto	Royal York	May 7–10
1963	Fall	New York	Commodore	September 10–13
1964	Spring	Detroit	Cadillac	April 28–May 1
1964	Fall	Chicago	Sherman	September 1–4

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Chairman: E. S. Kern (R. T. Vanderbilt, 230 Park Ave., N. Y.). *Vice-Chairman:* Henry J. Peters (Bell Telephone Labs., Murray Hill, N. J.). *Secretary-Treasurer:* M. E. Lerner (Rubber Age, New York). Terms end December 31, 1960. *Sergeant-at-Arms:* Clifford J. Lewis (U. S. Rubber Company, Passaic, N. J.). *Directors:* B. A. Wilkes, R. M. Glidden, L. J. Koch, L. C. Komar, W. J. O'Brien, E. C. Strube, A. H. Woodward, Bryant Ross, W. R. Hartman, M. A. Durakis, J. T. Dunn, J. E. Walsh, R. B. Carroll, R. G. Seaman. Meetings in 1960: March 25, June 9 (Summer Outing), Aug. 2 or 4 (Golf Outing), Oct. 21, Dec. 16 (Christmas Party); in 1961: March 24, June 8 (Summer Outing), Aug. 1 or 3 (Golf Outing), Oct. 20, Dec. 15

Northern California Rubber Group

President: Drace "Kut" Kutnewsky (Burke Rubber Co., San Jose). *Vice-President:* Claude "Corky" Corkadel (Oliver Tire & Rubber Co., Oakland). *Treasurer:* Joe Mattson (Witco Chemical Co., San Francisco). *Secretary:* Ray Brown (Burke Rubber Co., San Jose). *Directors:* Keith Large, Vic Carriere.

Philadelphia Rubber Group

Chairman: R. S. Graff (E. I. du Pont de Nemours & Co., Wilmington). *Vice-Chairman:* H. C. Remsberg (Carlisle Tire & Rubber, Carlilse, Pa.). *Secretary-Treasurer:* R. N. Hendrickson (Phillips Chemical Co., 2595 East State Street, Trenton, N. J.). *Executive Committee:* T. E. Farrell, R. N. Hendriksen, James Jones, George N. McNamara, H. M. Sellers, Merrill Smith. *National Dir.:* M. A. Youker (E. I. du Pont de Nemours & Co., Wilmington).

Rhode Island Rubber Group

Chairman: H. W. Day (E. I. du Pont de Nemours & Co., Boston). *Vice-Chairman:* Harry L. Ebert (Firestone, Fall River, Mass.). *Secretary-Treasurer:* W. J. Blecharczyk. *Historian:* R. G. Bolkman (U. S. Rubber Co., Providence). *Executive Committee:* E. S. Uhlig, R. B. Robitaille, J. M. Vitale, C. A. Damicone, G. E. Enser.

Southern Ohio Rubber Group

Chairman: R. J. Hoskin (Inland Mfg. Div., Dayton, Ohio). *Chairman-Elect:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio). *Treasurer:* J. M. Kelble (Wright Patterson AF Base, Ohio). *Secretary:* R. E. Wells (Precision Rubber Prod. Co., Dayton 17, Ohio). *National Director:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio).

Southern Rubber Group

Chairman: Warren Hall (Phillips Chemical Co., 318 Water Street, Akron, Ohio). *Vice-Chairman:* E. H. Ruch (Firestone Tire and Rubber Co., Memphis, Tenn.). *Secretary:* E. Strube (E. I. du Pont de Nemours and Co., Atlanta, Ga.). *Treasurer:* R. C. Whitmore (Better Monkey Grip Co., Dallas, Texas). Meetings in 1960: Feb. 12 and 13 Shamrock Hilton Hotel, Houston, Texas. June 10 and 11 (Altanta, Georgia). October 9 and 10 (New Orleans, La.); in 1961: January 20 and 21 (Dallas, Texas, Statler Hilton Hotel).

Washington Rubber Group

President: Robert Stiehler (National Bureau of Standards). *Vice-President:* A. W. Sloan (Atlantic Research, Alexandria, Va.). *Secretary:* George T. Richey (National Bureau of Standards). *Treasurer:* J. R. Britt (B. F. Goodrich Co.). *National Director:* A. W. Sloan.

Ontario Rubber Group

Chairman: O. R. Huggenberger (Dominion Rubber Co. Ltd., Montreal).

THE 76TH MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY AND THE INTERNATIONAL RUBBER CONFERENCE NOVEMBER 8–13, 1959

The 76th meeting of the division and the International Rubber Conference took place simultaneously Nov. 8 to 13 at the Shoreham and Sheraton-Park Hotels in Washington, D. C. The ACS Division of Rubber Chemistry, Committee D-11 on Rubber and Rubber-Like Materials of the American Society for Testing Materials, and the rubber and plastics division of the American Society of Mechanical Engineers were joint sponsors of the conference.

The Charles Goodyear Medal Lecture "People and the Banbury Mixer" was delivered by F. H. Banbury.

During the entire week there were exhibits of machinery and testing equipment used by the rubber industry, and displays of rubber products.

Dr. Wallace R. Brode, Science adviser to the Department of State spoke at the Authors' Breakfast.

General chairman of the meeting was A. E. Juve of the B. F. Goodrich Research Center. Chairman of the program committee was Dr. B. S. Garvey, Jr., Pennsalt Chemicals Corp. Dr. A. W. Sloan of Atlantic Research Corp. was chairman of local arrangements. Committees were as follows.

INTERNATIONAL RUBBER CONFERENCE COMMITTEES

Administrative Committee

A. E. Juve, Chairman
J. J. Allen, Secretary
A. W. Sloan
S. Collier
H. G. Bimmerman
R. G. Seaman
R. D. Stiehler
G. Bruggemeier
B. S. Garvey, Jr.

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B. S. Garvey, Jr., Chairman
R. G. Seaman, Secretary
J. D. D'Ianni
C. F. Gibbs
W. F. Tuley
G. C. Maassen
O. D. Cole
R. D. Stiehler
G. Bruggemeier
M. E. Lerner

The Local Committee on Arrangements

A. W. Sloan, Chairman
N. Bekkedahl, Chairman, Committee on Exhibits
H. C. Bugbee, Chairman, Committee on Plant Trips and Transportation
E. A. Bukzin, Chairman, Committee on Registration and Information and Card File
C. R. Collins, Chairman, Committee on Ladies' Entertainment
G. W. Flanagan, Chairman, Committee on Finance
R. H. Mattson, Chairman, Transportation Committee

G. B. Krantz, Chairman, Committee on Publicity
W. J. Sears, Chairman, Banquet Committee
R. D. Stiehler, Consultant to Local Committee on Arrangements
R. F. Tener, Chairman, Committee on Hotel Arrangements, Housing, and Meeting Rooms

The technical program consisted of 71 papers. These were published as a book called the "Proceedings"; the Foreword and Table of Contents from the Proceedings are reprinted in the section immediately following.

PROCEEDINGS OF THE INTERNATIONAL RUBBER CONFERENCE. A book consisting of 71 papers (616 pp.) presented at an International Rubber Conference, Washington, D. C., November 8–13, 1959. Obtainable postpaid at $10.00 by members and $12.50 by non-members of Division of Rubber Chemistry (318 Water Street, Akron, Ohio), or Committee D-11 on Rubber and Rubber-Like Materials, American Society for Testing Materials (1916 Rose Street, Philadelphia, Pa.), or Rubber and Plastics Division, American Society of Mechanical Engineers (29 W. 39th Street, New York 8, N. Y.). The Foreword and Table of Contents to the Proceedings are as follows.

FOREWORD

The committee which organized this International Rubber Conference was faced with the problem of deciding whether to publish a bound volume of the papers along with discussion as has been done by the Institution of the Rubber Industry for the three international conferences which have been held in London, or to follow some other pattern.

After much discussion, it was decided that the papers would be preprinted in a single, relatively inexpensive vound volume which would be provided each member of the conference at the time of registration. This procedure has certain advantages as well as disadvantages. The most important of the former is that the costs could be kept in reasonable bounds, and the most important of the latter is that no permanent record of the discussion from the floor will be available.

This decision in turn created some problems. It was necessary that all finished manuscripts be available sufficiently early so that editing could be done well in advance of printing. The tendency of authors to procrastinate is well known, and the problem of activating them to submit their manuscripts was a real one. Unfortunately, several of the original titles were cancelled for this reason. The problem of editing the papers was also a difficult one. The Program Committee under the chairmanship of B. S. Garvey, Jr., which was responsible for these activities, has done an excellent job. Inevitably, there will be errors, but these we feel will be relatively insignificant.

It was also necessary to decide how and by whom this volume should be published. A committee headed by R. G. Seaman and including R. E. Hess of the staff of the American Society for Testing Materials and James M. Crowe of the staff of the American Chemical Society studied this problem at some length and decided that the ACS would handle production of the book in the size, form and manner in which you find it. Much credit is due Mr. Crowe and his staff for their efforst in preparing these "Proceedings" for publication.

This volume is the culmination of the efforts of these several groups and, of course, the efforts of the authors of the papers without which there would be no volume and no conference.

A. E. JUVE, Chairman, International Rubber Conference Committee

E. H. KRISMANN, Chairman, Division of Rubber Chemistry, American Chemical Society

S. COLLIER, Chairman, Committee D-11, American Society for Testing Materials

R. D. STIEHLER, Chairman, Rubber and Plastics Division, American Society of Mechanical Engineers

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NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY. Volume XXII. 1958. Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 4 Kensington Palace Gardens, London, W 8, England. Hard cover, $9\frac{1}{2} \times 7$ inches, 125 pages. Price: $3.50—The twenty-second report on British rubber technology covering developments during the past year does not depart essentially from the pattern set by its predecessors. However, a careful perusal of the chapters contributed by two dozen specialists in the major areas of rubber research and manufacture reveals some new shifts of focus. This is the first report to offer a section on the manufacture of synthetic rubber. Altogether, this report is an outstanding example of succinct, well-written reporting comprehensively documented by citations and statistics. [Reviewed in *Rubber Age.*]

Beginning with the July issue, the *Journal of Polymer Science* has been publishing abstracts, in English, of all articles as they are published in issues of the new Russian journal devoted to polymers, *High Molecular Weight Compounds* (*Vysokomolekularnye Soedineniya*). The first issue of the new bimonthly journal appeared in May. Professor V. A. Kargin is editor-in-chief and is assisted by P. V. Koslov and H. C. Kolesnikov.

RUBBER RED BOOK. Edition 12. 1959. Edited by M. E. Lerner. Published by *Rubber Age*, 101 West 31st Street, New York 1, New York. Paper cover, $8\frac{1}{4} \times 11\frac{1}{4}$ inches, 854 pages. Price $15.00.—This book, essentially a directory of the rubber industry, is published for the first time on an annual basis and is changed to a larger directory-type format. There is little change in the organization of the book from previous editions; each section, however, has been compiled from freshly secured data and represents new and up-to-date information. Fourteen additional manufacturers and 47 additional plants have added to this edition. The coverage of the industries and its suppliers is excellent. The book is recommended for most technologists, purchasing agents, and sales organizations to the rubber industry. [Reviewed in *Rubber World.*]

ELSEVIER'S RUBBER DICTIONARY. Compiled by Rubber-Stichting, Delft, Netherlands. Distributed by D. Van Nostrand Co., Inc., 120 Alexander Street, Princeton, New Jersey. Hard cover, 6×9 inches, 1537 pages. Price: $60.00.—One of the most ambitious projects in the recent polyglot publishing cycle has now been offered to the rubber engineer and technician in the form of a dictionary in ten languages: English, French, Spanish, Italian, Portuguese, German, Dutch, Swedish, Indonesian, and Japanese.

Nearly 8000 entries cover virtually every aspect of laboratory, office and field terminology from botany to shoe manufacturing. The basic word list is in English, distinguishing American from British usage in order to tell "trucks" from "lorries" and "suspenders" from "braces". The corresponding terms in the other nine languages are then listed horizontally across two pages, according to a system proposed by the United Nations Educational, Scientific and Cultural Organization. In the second part of the dictionary, thumb-indexed alphabetical lists for each language give numerical keys to the basic English

table. This original arrangement, facilitating swift reference, constitutes a distinct advance over previous vertical layout of multilingual dictionaries.

The former staff of Rubber-Stichting, the Dutch Rubber Foundation, has done an outstanding job in what must have been an extremely time-consuming, laborious project. It was materially assisted by rubber institutes in various countries whose languages were included. The only major gap in comprehensiveness is the absence of Russian, particularly in the light of current Soviet literature exchanges. Minor defects in the binding and occasional typographical errors do not detract from the dictionary's usefulness for all those working and dealing in rubber, whether in connection with research, management, production, or overseas trade. [Reviewed in *Rubber Age.*]

TIRE DYNAMICS. By Andrew J. White. Published by Motor Vehicle Research, Inc., South Lee, New Hampshire. Hard cover, 8 × 11 inches, 268 pages. Price: $15.00.—This reference work, primarily intended for lawyers and automobile accident investigators, reports on field studies of the relationship between tread stock materials of tires and stopping distance of passenger car vehicles under locked-wheel conditions. It is the result of five years' research costing a quarter of a million dollars and testing virtually all available makes of tires and automobiles.

In the process, the study arrives at some surprising conclusions. It explains, for example, why tire mark measurements cannot be related to vehicle speeds; shows that some retread tires can stop a vehicle faster than new premium tires, and indicates that smooth tires can stop a car faster than new ones on a dry roadway.

Nearly 400 photographs, tables, drawings and charts illustrate the text, permitting a graphic understanding of all phases in the test procedures. Extremely accurate measurements were obtained by a method in which a colored chalk charge was fired from a pistol at the roadway by a mechanism triggered the moment the brake pedal was depressed. Despite its legal emphasis, this book's scientific and technical data on tires makes it rewarding reading for anyone in the industry. [Reviewed in *Rubber Age.*]

SOURCE BOOK OF THE NEW PLASTICS. Volume I. Edited by Herbert R. Simonds. Published by Reinhold Publishing Corp., 430 Park Avenue, New York 22, New York. Hard cover, 6 × 9 inches, 354 pages. Price: $10.00.—Sixty plastics producing companies have contributed articles describing their new materials to this reference work which reports developments as late as the summer of 1959. The brief introduction is followed by a report on improvements in established materials such as epoxy resins, vinyls, urethane foams, and acrylo-nitrile-butadiene-styrene. The chemical and physical properties of four elastomers—stryene rubber, neoprene, natural rubber and polyurethane—are outlined in a comparison chart. A section on silicone rubber deals with the latest room temperature vulcanizing compounds and discusses fabrication techniques. An "Introduction to Polypropylene" explains Professor Natta's work and the earlier German development of stereospecific catalysts. A report on graft copolymers describes the use of that technique in modifying plastic properties.

While the contributions naturally vary in clarity and explicitness, the editors are to be commended for compiling such an up-to-date source book. [Reviewed in *Rubber Age.*]

THE SYNTHETIC ELASTOMERS AND THEIR MAIN APPLICATIONS. By G. D. Lefcaditis. Published by Imprimerie Nestia, Athens, Greece. 72 pages.—This Greek-language publication describes the nature and the preparation of the various elastomers along with the properties and applications of their vulcanized compounds. The author, chief chemist of Karthea Rubber Manufacturing Co., Athens, discusses both hot and cold polymerized SBR polymers including oil-extended grades and black masterbatches. He also has included sections on oil- and solvent-resistant rubbers, the Vulcollans, Adiprene, arctic rubbers, Hypalon, Kel-F, "Viton," and many other of the newer materials. [Reviewed in *Rubber World.*]

THE TENSILE STRENGTH OF ELASTOMERS ACCORDING TO CURRENT THEORIES

F. BUECHE*

DEPARTMENT OF PHYSICS, UNIVERSITY OF WYOMING, LARAMIE, WYOMING

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I. INTRODUCTION

Perhaps no property of rubbers has been more widely measured than has tensile strength. Its practical importance is obviously great. Consequently a large amount of research effort has been directed toward the development of high tensile strengths in rubbers. This fact notwithstanding, it still remains true that the molecular mechanisms responsible for the observed tensile strengths of rubbers are, for the most part, only vaguely understood.

It is the purpose of this review to present current thinking concerning the molecular basis for the tensile strength of rubbers. The molecular pictures presented should be viewed as their proponents view them, as tentative approximations which must be greatly extended and modified as our understanding increases. We shall strive in this review to point out the basic molecular factors involved and the ways in which present theories have approached them. Emphasis will be placed on the ideas rather than the mathematical details with the understanding that those who are interested in the details of the various calculations will refer to the original literature.

II. A PERFECT NETWORK

We can gain considerable insight into the problem of tensile strength by considering a perfect (but nonattainable) rubber network. It consists of a cubical network of chains one cube of which is pictured in Figure 1. We assume each network chain (i.e., the chain between crosslinks) to be of molecular weight M_c and originally oriented in space as shown in Figure 1. Con-

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sequently, under a vertical tensile stress the vertical chains will be stretched identically and the horizontal chains will be compressed.

Upon stretching such a simplified rubber, the entire load must be held by the vertical chains. If there are n vertical strands in the sample of unit original cross sectional area and if each chain can hold a load F_c, the sample will be capable of holding a load given by

$$TS = nF_c \tag{1}$$

In this and all subsequent statements, TS is meant to represent the tensile strength referred to the original unstressed cross section.

The quantity n is easily obtained by the following line of reasoning. If the sample is actually a one cm cube, there will be as many Z directed strands, n, as there are X or Y directed strands. Consequently, the total number of strands is merely $3n$.

However, each strand will contain p network chains, each of molecular weight M_c. Therefore, the total number of network chains per cc is just $3pn$. But since M_c grams of rubber must contain a number of chains equal to Avo-

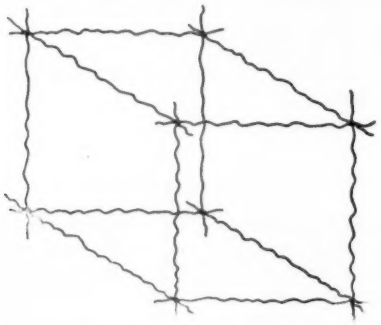

FIG. 1.—A schematic network model used in Section II.

gadro's number N, one cc will contain $\rho N/M_c$ network chains where ρ is the density of the rubber. Thus one has

$$3pn = \rho N/M_c \tag{2}$$

In addition, a direct count of the number of network chains per cc, in the case of the model of Figure 1, gives $3p^3$. Therefore, we also have

$$3p^3 = \rho N/M_c \tag{3}$$

Combining Equations (2) and (3) allows us to solve for n. After substituting this value in Equation (1), one has for the tensile strength

$$TS = (\rho N/3M_c)^{\frac{1}{2}}F_c \tag{4}$$

This simple expression for tensile strength is in gross error. For example, when $M_c = 1000$ the above equation predicts a strength of about 50,000 psi if

reasonable values for the density ρ, and bond strength F_c are used. This value is at least ten times larger than experimental values. Obviously the approximations made in this calculation have been too severe. Let us enumerate the major ones:

1. All the rubber molecules in the sample are bound into the network. Chain ends are ignored.
2. All network chains are exactly the same length.
3. One third of the chains point in the Z direction and similarly for the X and Y directions.
4. Flaws in the sample are ignored.
5. The possible existence of crystallinity is ignored.
6. All viscous time effects have been neglected.

The effects of these approximations will be considered in that which follows. As of the date of this review, the theories now available do not refine any of these approximations in a wholly acceptable fashion. However, each of the three theories discussed below does succeed in reducing the importance of at least one of these approximations.

III. THE THEORY OF A. M. BUECHE [1]

A. M. Bueche has presented a more refined theory which removes some of the objections to the treatment of Section II. His approach is to obtain an expression for the tensile strength in terms of other physical properties of the rubber without going into exact detail about the mechanisms involved. The advantage of such an approach is crudely shown if one considers that very strong rubbers must necessarily have a high modulus near the rupture point. For this reason, it might be possible to relate tensile strength to the modulus without going into detail about the processes involved. As a result, a rather accurate relation between the easily measured quantity, modulus, and tensile strength might result.

Bueche approached the problem by first setting up a macroscopic criterion for rupture. He considers a tensile test for which the rate of elongation is $(\partial\alpha/\partial t)$ with $\alpha = L/L_0$ where L and L_0 are the stretched and initial lengths of the sample respectively. Under such conditions most stress-strain curves will show a single maximum stress, τ_0, at which point (indicated by subscript c)

$$(\partial\tau/\partial t)_c = 0 \tag{5}$$

The stress at this point on the curve will be the tensile strength of the sample.

He then makes use of the fact that as a first approximation at least

$$\tau = n\phi(\alpha) \tag{6}$$

where $\phi(\alpha)$ is a function describing the shape of the stress-strain curve in the absence of chain breakage. For low elongations, the theory of rubberlike elasticity gives[2]

$$\phi(\alpha) = \alpha - 1/\alpha^2 \tag{7}$$

The quantity n corresponds to the number of vertical strands used in the previous section. However, Bueche does not make this exact identification since he takes n to be the number of bonds crossing a cross section plane in the sample.

If one takes the time derivative of Equation (6) and sets it equal to zero in Equation (5) so that conditions at the breaking point are assumed, one finds

$$-\left(\frac{1}{n}\frac{\partial n}{\partial t}\right)_c = \left(\frac{1}{\phi}\frac{\partial \phi}{\partial \alpha}\right)_c \left(\frac{\partial \alpha}{\partial t}\right)_c \tag{8}$$

This is now an expression relating the relative rate of breaking of bonds in the sample at the rupture point to the product of (1) the relative slope of the ideal stress-strain curve and (2) the rate of elongation.

The second of these two quantities can be measured easily in a given tensile test. The first can be estimated rather closely either from an application of Equation (7) (more ideally from the James-Guth equation[3]) or from stress-strain measurements prior to the onset of breakage. If one could find an expression for the rate of chain breakage $\partial n/\partial t$, Equation (8) should then provide a useful relation between the various tensile properties of rubber.

Bueche assumes that the relative rate of chain breakage is expressible from the usual reaction rate theory as

$$-\left(\frac{1}{n}\right)\left(\frac{\partial n}{\partial t}\right) = (kT/h)\exp\left[-(\Delta F^*/RT) + (\Delta F/RT)\right] \tag{9}$$

where ΔF^* is the free energy of activation for the bond breaking process. The quantity ΔF is taken with respect to the unstretched, uncrosslinked rubber and is the free energy gained upon crosslinking and stretching. An estimate may be made for ΔF^* from the results of stress relaxation measurements involving chain scission or from other considerations. Therefore, only the computation of ΔF remains.

The entropy of a rubber is changed in a known way upon crosslinking and deformation[2]. In addition, the enthalpy of the system ΔH will change during the crosslinking process. Adding these contributions to the free energy change, one then has an expression for ΔF. For each mole of primary chains it is

$$\Delta F = \Delta H + RT\int_{\alpha=1}^{\alpha=\alpha_c} \phi(\alpha)d\alpha + \text{const.} \tag{10}$$

The constant in this equation is essentially known since it involves only the product of the gas constant with the temperature, RT, and the number of segments in a chain.

After combining Equations (8), (9) and (10), Bueche arrives at a relation involving the several quantities used in these equations. He tested the resulting equation using data on silicone rubber and found that it was reasonably satisfactory. For example, treating all quantities except ΔF^* and ΔH as known, he computes reasonable values for these quantities although ΔH is found to be somewhat larger than expected.

It is seen that Bueche's approach minimizes many of the approximations inherent in the method of Section II. He is able to make a direct correction for the effects of chain ends as will be pointed out later. The chain details involved in approximations 2 and 3 of the previous section are largely eliminated through the use of the function $\phi(\alpha)$. There is some possibility that the effects of flaws, crystallinity, fillers, and viscous effects could also be incorporated into this treatment, although nothing has been done in this regard to date.

On the other hand, this treatment is not as nice as might be desired simply because it does not give an explicit value for tensile strength in terms of molecular quantities. Values from the measured stress-strain curve are needed. In addition, by ignoring the actual molecular details of the breaking process, it casts little light upon these processes.

IV. THE THEORY OF TAYLOR AND DARIN [4]

The theory of Taylor and Darin[4] is more explicit in its treatment of the molecular basis for tensile strength of rubbers. It initiates by assuming what seems to be a reasonable functional relationship between tensile strength and various molecular factors, viz.

$$TS = K \text{ (total number chains/vol)} \cdot \text{(fraction orientable chains)} \cdot \text{(orientation factor)} \quad (11)$$

In this expression, the constant K is an unknown parameter which must depend upon the bond strength among other things. The total number of chains per unit volume is proportional to $[(1/M_n) + (1/M_c)]$ where M_n is the number average molecular weight of the primary chains[5]. The fraction of orientable chains is taken to be the same as Flory's expression[5] for the fraction of "active" chains, i.e., those chains bound to the network at two ends. This value is $[1 - (2M_c)/(M_n + M_c)]$. It should be noticed that in the simple theory of Section II the value of M_n is taken to be infinite and this factor is then unity.

The real heart of this theory is the evaluation of the "orientation factor" in Equation (11). Taylor and Darin make the plausible argument that only the most highly oriented chains will be of much importance as far as tensile strength is concerned. This is reasonable if one recalls that near the breaking point a chain is nearly fully elongated and holds many times the load which is needed to extend it to three-fourths of its maximum length.

Taylor and Darin, therefore, define the orientation factor to be the fraction of chains oriented at less than a very small angle δ to the direction of stress at the instant of breaking, i.e., the fraction of chains nearly in line with the stress. If one assumes an affine deformation with an extension ratio at break of α_B one can show that this fraction is just $[1 - (1 + \delta^2\alpha_B^3)^{-1}]$.

Upon substituting these quantities in Equation (11) and after combining the constants into K, one finds

$$TS = \frac{K}{M_n}\left(\frac{M_n}{M_c} - 1\right)[1 - (1 + \delta^2\alpha_B^3)^{-1}] \quad (12)$$

In order to compare this expression with experiment one must have data for the tensile strength as a function of M_n or M_c or both. The values of α_B, the extension ratio at the breaking point must also be known. One can then try to fit the data by choosing proper values for K and δ.

Taylor and Darin compared Equation (12) with their measurements for the tensile strength of a purified sample of SBR as a function of degree of cross-linking. They assumed M_n to be 120,000, which is too high for the number average molecular weight of raw SBR, but which is probably nearly correct for their extracted rubber. The agreement between experiment and their theory is shown in Figure 2 and is seen to be quite good. Although the theoretical

curve drops too rapidly at high degrees of crosslinking, the general shape of the curve is correct.

The value needed for δ in order to fit the experimental data is 0.4°. This value is indeed very small and tends to confirm the original assumption that the major portion of the load is held by the most highly oriented chains. Not much can be concluded from the value needed for the parameter K since its exact physical significance is unknown.

As pointed out by Taylor and Darin, the greatest drawback to the use of their theory is the fact that α_B must be known from experiment. An effort was made by Taylor and Darin to derive an expression for α_B from molecular considerations but the result was not very satisfactory. Although their treatment gave the exact value for α_B at one value of M_c, it was in error by a factor of 3 when M_c was decreased by a factor of 3. Since α_B appears to the third

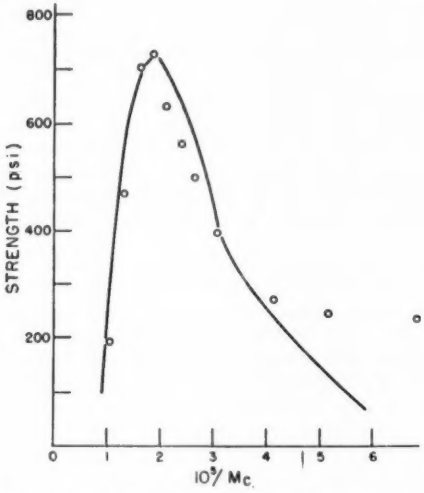

FIG. 2.—Taylor and Darin's data for SBR[4]. The curve is a plot of Equation (12) assuming $\delta = 0.4°$.

power in Equation (12), it is apparent that, as of now, α_B must be obtained from experiment.

Taylor and Darin also tried to extend their theory to include the effects of crystallization. This amounts essentially to making some intuitive guesses about how the factors in Equation (11) will change with crystallinity. Although some measure of agreement was found with the meager experimental data suitable for testing this point, the rather arbitrary nature of this phase of the treatment leaves much to be desired. However, certain aspects of their treatment of crystallinity must be correct and will be mentioned later.

These same authors also speculate upon the nature of the actual breaking process although these details should influence only the parameter K. They speculate that the rapid break is the result of an autocatalytic effect wherein the free radicals formed when one chain breaks propagate a breaking reaction through the sample. This reviewer is in grave doubt as to the acceptability of

this mechanism and, since it is not an intimate part of the theory, will not pursue it further.

In summary, then, the theory of Taylor and Darin is quite successful in duplicating the experimental data for tensile strength. This success is partly the result of the fact that the relative elongation at break α_B as determined from experiment, is used to conceal a certain lack of knowledge concerning the molecular mechanisms involved. In addition, the parameter K is almost purely arbitrary and allows considerable freedom in adjusting theory to experiment. However, the other parameter δ must (and does) satisfy certain restrictions. It would appear that, in spite of its obvious shortcomings, this theory contains a good deal of truth and represents a significant advance in our understanding of the molecular variables involved in determining tensile strength.

V. ANOTHER APPROACH [6]

Perhaps a more acceptable way to attack the problem of tensile strength is to go back to the basic chain structure and proceed from first principles. This is, of course, the approach outlined in Section II. The model used there, however, was too crude in its representation of any actual molecules. A more realistic (and complicated) approach is needed. This means that the simplifications listed for that model should be eliminated or at least minimized. The present section will be devoted to the task of extending the model of Section II to include the effects of unequal network chain lengths and the influence of crystallinity and fillers.

If one refers to Figure 1, it is easily seen that if one of the vertical network strands possesses fewer monomer units than the average, that strand will hold more than its share of the load. This means that such a strand will break before the average strand has approached its load limit. It is not a simple matter to compute the variations in load among the vertical strands in an actual rubber. Until now, the computation has only been done approximately and then only for the case of a simplified system with nonrandom orientation of chains.

To a first approximation it can be shown[6] that the probability P that a given vertical network chain will experience a load greater than F_c when the average load per chain is F, is given by

$$P \sim \exp\{-(\text{const.})[(F_c/F) - 1]^2\} \tag{13}$$

This expression allows one to compute the number of chains which will break under a given tensile load. It does not present the whole picture of the processes involved, however, since it ignores the fact that when one chain breaks it may cause another to break. In fact, the almost instantaneous process of sample rupture may be thought of as being the result of a vast avalanche of chain failures caused by the initial rupture of a single chain.

The mechanism of this chain reaction was thought by Taylor and Darin to involve the action of free radicals as pointed out in the last section. This reviewer believes, however, that it is simply a mechanical process involving the fact that when a chain breaks, the load it held must be added to the loads already held by the neighboring chains. For example, the schematic representation of a tetrafunctional network shown in Figure 3, if the central chain breaks at x, the load held by that chain will be thrown onto the two adjoining chains. If, on the average, the new load on either one of these chains exceeds F_c, the

neighbor chain will also break, causing another to break and so on. Therefore, the break will propagate and the sample will rupture.

From this line of thought it appears that the rubber will fail when the external stress becomes large enough so that when a chain breaks this will cause, on the average, at least one other chain to break. If we assume the sample to be tetrafunctionally crosslinked, it is probably a fair approximation to say that an extra load $0.5\ F_c$ is thrown onto each of the two neighbor chains when a given chain breaks. It is then possible, using this criterion for break, to show that Equation (13) gives rise to the following expression for the tensile strength

$$TS = (\nu_e/3)^{\frac{1}{3}} F_c[1/(1 + 0.61X) - \tfrac{1}{2}] \tag{14}$$

with

$$X \equiv 2(aF_c/kT\sigma)^{\frac{1}{3}}$$

The quantity ν_e is the effective number of network chains per unit volume and for infinite molecular weight is the total number of network chains $\rho N/M_c$ as found in Section II. If there are σ possible crosslinking sites in a network

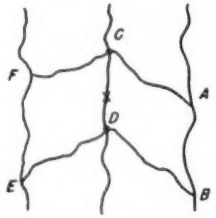

FIG. 3.—A schematic network model used in Section V.

chain of molecular weight M_c, then a is the length of chain associated with each one of these sites.

It should be noted that the tensile strength given by Equation (14) differs in an important way from the assumption of Taylor and Darin given in Equation (11). The number of network chains per unit volume enters here raised to the two-thirds power rather than to the first power. Unfortunately, data presently available are not accurate enough to test this point. From a theoretical viewpoint, the two-thirds power dependence appears to have more justification than does the first power dependence.

To test Equation (14) against experiment it is necessary to replace ν_e by $(\rho N/M_c)(1 - 2M_c/M_n)$. The first factor was obtained for an infinite molecular weight rubber in Section II. The second factor is an approximation to the fraction of chains which are tied to the network at both ends. Unfortunately, this expression for the chain end correction is not valid when M_c is close to M_n but it is probably sufficiently accurate for most purposes. In addition, it does not take into account the fact that some network chains will not be fully effective merely because they are close to a network chain which contains a chain end. Equation (14) then becomes

$$\begin{aligned} TS &= \tau_0 X^{\frac{1}{3}}[1/(1 + 0.61X) - \tfrac{1}{2}][1 - (2M_c/M_n)]^{\frac{1}{3}} \\ \tau_0 &= (\rho N/3M_0)^{\frac{1}{3}}(kT/4aF_c)^{\frac{1}{3}}F_c \end{aligned} \tag{15}$$

where M_0 is the molecular weight associated with each crosslinking site.

Equation (15) contains two adjustable parameters; the strength of an individual chain F_c, and the length of a chain segment a. The data of Taylor and Darin[4] for SBR can be fitted by Equation (15) provided these two parameters are chosen judiciously. The result is shown in Figure 4. It is found that the values needed for a and F_c are reasonable in size and so Equation (15) appears to be significant. It does not, however, represent the data well at high degrees of crosslinking. In fact, it is inferior to the result obtained by Taylor and Darin in this respect, i.e., Equation (14).

The cause of the inadequacy of Equation (15) at high crosslinking is probably the result of the assumption concerning the redistribution of load when a chain breaks. When the crosslinks are very close together it is probable that the extra load will be held by more than two neighbors. This fact will decrease the chance that the neighbor will break and the tensile strength given by Equation (15) will be too low.

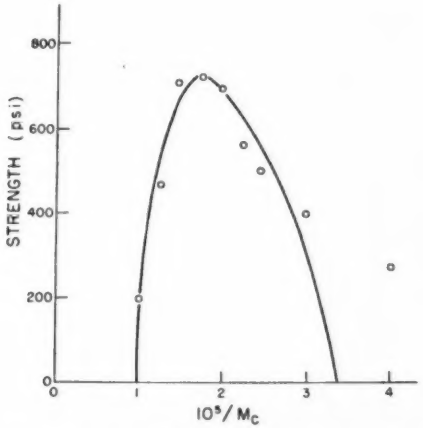

FIG. 4.—Comparison of the data of Taylor and Darin for SBR[4] with the result predicted by Equation (15).

It might be worth pointing out that the basic difference between the theory of this section and that of Section II is the introduction of unequal stresses among the vertical strands. Consequently, the result of this section predicts a tensile strength much lower than is obtained assuming equal sharing of the load among the strands. Some experimental justification for the belief that unequal stresses are important in lowering the strength can be found in the case of the metal oxide vulcanizates of the carboxylic rubbers[7]. These rubbers are thought to have mobile crosslinks which allow the most highly stressed chains to relax and share their load with neighboring chains. The strength of these gum stocks is found to be much higher than for any other similar noncrystalline rubber.

It is also of interest to notice that the primary number average molecular weight of the rubber M_n is important as far as strength is concerned. This is shown in Figure 5 where the tensile strength predicted by Equation (15) is plotted assuming various values for M_n. In the same figure are shown some experimental points[8] for SBR 1006. Obviously this gum stock has a considerably

lower M_n than does the extracted rubber measured by Taylor and Darin[4]. It would appear that even SBR gum stocks could give tensile strengths near 1800 psi if the molecular weight were high enough.

In spite of the failure of Equation (15) at high degrees of crosslinking, it has considerable merit because of its more detailed treatment of the molecular mechanisms involved. It is possible to compare the two parameters in the equation with physical quantities in order to test their validity. This test appears to confirm the model upon which Equation (15) is based. In addition, it will be seen that the explicit nature of this model allows one to extend it to rubbers containing fillers and crystallites.

Aside from the failure of Equation (15) at high degrees of crosslinking, it possesses other inadequacies which are relatively obvious. First, it is based on a molecular model which makes use of only a crude approximation to the true random orientation of the network chains. This complication could presum-

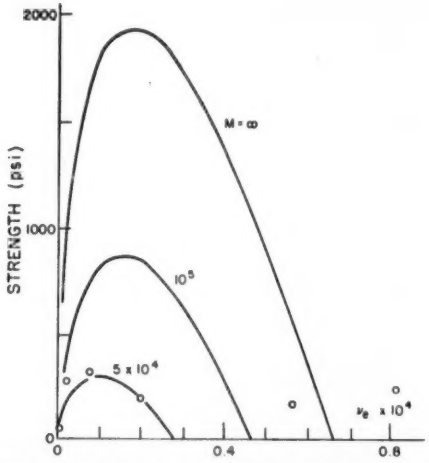

FIG. 5.—Variation of tensile strength with number average molecular weight as predicted by Equation (15). The points are experimental data for SBR gum stock.

ably be included in the model but as of now it has not been done. Second, the model assumes equilibrium conditions and any variation of tensile strength with rate of test is excluded. This topic has been investigated to some extent and will be discussed further in a later section. Third, the influence of fillers and crystallites is not included. Some work on this subject has been done and is discussed in the next section.

VI. THE EFFECTS OF FILLERS AND CRYSTALLITES

The tensile strengths of rubbers which crystallize upon stretching are known to be much higher than noncrystallizable gum stocks. For example, natural rubber gum stocks show tensiles in the neighborhood of 4000 psi whereas SBR tensiles are near 500 psi. This fact has been the topic of considerable speculation.

A. *Flory's interpretation.*—Flory[9] interpreted his data for natural rubber, shown in Figure 6, in terms of crystallization upon stretching. The explanation he gives for the maximum in the tensile strength curve has to do with the fact that the tendency to crystallize will decrease with an increasing number of crosslinks. If one assumes that this effect is large, the strength will decrease at high degrees of crosslinking.

Although such an explanation seems reasonable at first sight, the fact that Taylor and Darin's data for noncrystalline SBR show the same behavior with increasing crosslinking leads one to believe that Flory's explanation may not be correct. There is no compelling reason to believe that Flory's mechanism is very important at the crosslinking degrees normally encountered. Its true importance is not known at this time, however. The fact that behavior observed for natural rubber may be rather closely predicted by the theory of Section V without recourse to Flory's mechanism, as will be seen below, indicates that it may be of secondary importance.

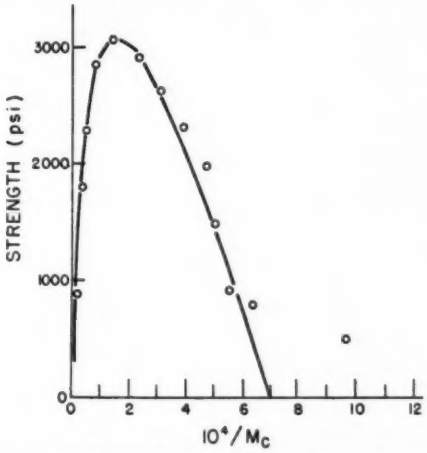

FIG. 6.—Tensile strength of natural rubber (Flory[9]). The solid curve is a plot of Equation (15).

B. *Taylor and Darin's procedure.*—Taylor and Darin[4] introduce the effects of crystallinity in a more or less intuitive fashion by considering two of its effects. First, the crystallites act as additional crosslinks and therefore increase the crosslink density. This fact in itself would probably be of only minor consequence since the number of such pseudo crosslinks will be only a small percentage of the total at ordinary degrees of crosslinking. The second modification introduced by Taylor and Darin was to stipulate that all the chains in crystallites are within the angle δ and are therefore heavily stressed. This assumption will lead to an increase in tensile strength with crystallinity since the number of load holding chains increases in proportion to the degree of crystallinity.

To test Taylor and Darin's result one must have a knowledge of the percent crystallinity and the elongation at rupture for the rubber. Such data are very meager. Using the data available, it was found[4] that the theoretical relation predicted a maximum much like that shown in the curve of Figure 6. However,

it appears that the maximum predicted is too broad although this is not certain. Such behavior would be expected if the decrease in crystallization with increasing crosslinking were of only secondary importance. More experimental work is needed before a definite decision can be made on this point.

C. *A load-sharing mechanism.*—It is a striking fact that the tensile strength of noncrystallizable SBR rubber increases by nearly a factor ten when carbon black is dispersed in the rubber at a concentration of about 25%. Even more astonishing is the fact that the tensile strength vs. degree of crosslinking curve for such a loaded rubber, shown in Figure 7, looks much like the similar curve for natural rubber gum stock shown in Figure 6. This tends to indicate that the carbon black particles and rubber crystallites serve the same purpose.

If one accepts the interpretation for the action of crystallites presented by either Flory or Taylor and Darin, it is difficult to see what connection could

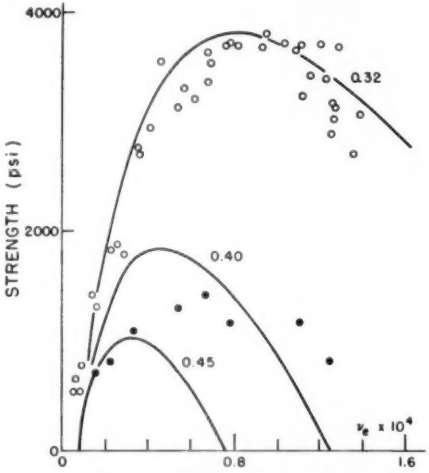

FIG. 7.—Tensile strength of SBR 1500 containing 30 parts HAF black at two temperatures, 23° C (open points) and 75° C (full points). The curves are plots of Equation (15) with the factor 0.5 replaced by the values indicated on the curve[6].

exist between the actions of filler particles and crystallites. This fact tends to detract from the creditability of these interpretations. It remains yet to show that another major mechanism is operating which is as applicable to filler particles as to crystallites. This may be done by extending the considerations of Section V[6,8].

It will be recalled that the rubber will break when, on the average, the breaking of one network chain causes one or more other network chains to break. This process of successive breaks is the result of the fact that the load held by a given chain must be taken on by its neighbors if the chain breaks. In Section II it was assumed that only the two nearest neighbor chains supported this extra load. Such will not be the case if filler particles or crystallites are present. This fact may be seen from a consideration of Figure 8.

If the central chain in Figure 8 breaks, the chain will relax and the load it previously held must be taken up in other ways. In the absence of crystal-

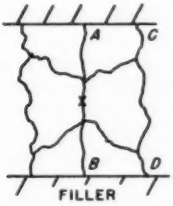

FIG. 8.—A diagram to illustrate the action of filler particles and crystallites.

linity and filler, the extra load would be mostly thrown onto the two adjacent chains. However, in the case illustrated, the broken chain will retract against the crystal or filler particle in such a way that only a slight extra load is imposed upon these two adjacent chains. Consequently, the break will not propagate through the sample until much larger loads have been applied to it and the strength will therefore increase as crystallites or filler are added.

The above idea can be incorporated into the theory outlined in Section V by stipulating that the load released by a breaking chain is shared by q, rather than 2, neighbors. When this is done, the factor of 0.5 in Equation (15) is replaced by $1/q$ and the rest of the equation is left unchanged. The variation of tensile strength with degree of crosslinking predicted by Equation (15) for various values of q is shown in Figure 7 together with experimental data for filled SBR at two temperatures. It will be noticed that the modified theoretical relation shows the expected features, although the agreement is far from perfect. The

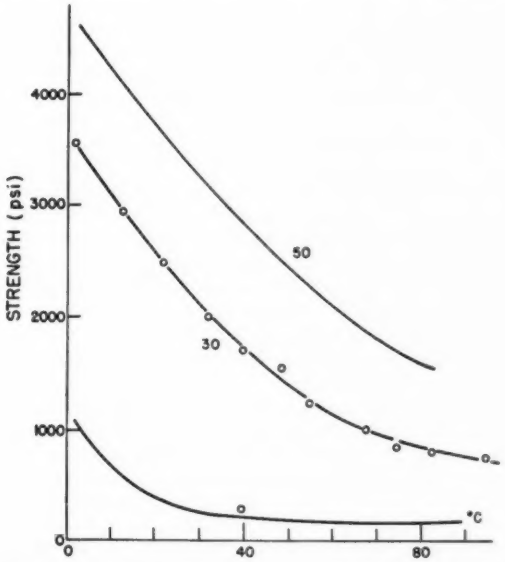

FIG. 9.—Variation of tensile strength of SBR 1006 with temperature. The numbers on the curves give the concentration of HAF black in parts per hundred of rubber.

data of Figure 6 for natural rubber can likewise be represented rather adequately by this relation.

As shown in Figures 7 and 9, the tensile strength of filled SBR decreases markedly with increasing temperature. Experiments using other fillers have shown[8] that the adhesion of the rubber to the filler decreased in step with the decrease in tensile strength. This indicates that the filler is ineffective if the rubber does not adhere well to it. Such behavior is to be expected if one accepts the load sharing mechanism for the filler action. It is obviously necessary that the rubber adhere to the filler if this mechanism is to be operative. Although the surface area and degree of dispersion of the filler is also important for this mechanism, the most important factor would appear to be the adhesion between the rubber and filler. A great deal of work has been done with various carbon blacks to determine their effectiveness in raising the tensile strength. The investigations of Kraus[10] are probably the most complete.

Although the load sharing mechanism for the action of fillers and crystallites appears to be moderately successful in interpreting the effects of these factors, the theory involved is still extremely crude. A more complete theory would actually evaluate q in terms of the size and number of the filler particles or crystallites. It is quite likely that q itself will vary with degree of crosslinking. In addition, the mechanisms of Flory and of Taylor and Darin are certainly operative to some extent and should be included in any complete theory. While it is probably true that the load sharing mechanism is the most important of those mentioned here, considerable work is needed to determine its true validity.

VII. IMPORTANCE OF EXTENSION RATE AND GLASS TEMPERATURE

It has been known for many years that the tensile strength of rubber varies markedly with the rate of test under certain conditions. The most complete investigation of this effect for SBR appears to be that of Smith[11]. He measured the tensile strength for this essentially amorphous rubber using strain rates in the range 0.16×10^{-3} to 0.16 sec^{-1} through the temperature range -34 to $+93°C$. He was able to correlate the results at various temperatures by the use of a temperature-time superposition procedure. His reduced data cover a very wide range of test rates as shown in Figure 10. The strength of this gum stock was about 230 psi at 25° C and at an extension test rate of 2 inches per minute.

The tensile strength is observed to rise markedly at very high test rates. Since it was found that a temperature-time superposition was apparently valid, this also means that the strength increased markedly at low temperatures. Both of these facts are known to be true not only for SBR but also for other rubberlike materials. They may be shown to be the result of the way in which the friction forces act within the rubber to retard the elongation of the network chains.

If one ignores the fact that true viscous flow may occur during very slow tests, the behavior may be explained somewhat as follows. At low strain rates the molecular network chains need move only very slowly as the sample is extended. The viscous forces, being proportional to the speed of the chains, will be very small. In addition, the chains will not lag far behind their equilibrium elongation for the stress present at any instant. The chains will therefore exhibit the strength which is characteristic of their extended, essentially motionless state. This is exactly the condition which has been presupposed in previous sections.

It is clear from this that the tensile strength should be constant at all low rates of test provided the rubber is warm enough so that the chains are reasonably free to move. Exceptions to this generality can usually be traced to true viscous flow within the rubber or to crystallization phenomena. Fortunately, the usual strain rates employed in the testing laboratory are low enough to be near this insensitive range at least in the case of the common rubbers. This would not be true, as will be seen, if the testing tempreature were twenty centigrade degrees lower or if the rubber had a glass temperature twenty degrees higher.

As the speed of the test is increased, or as the temperature is decreased, the chains will have increasing difficulty elongating as fast as the test requires. This is true since at higher strain rates the chains must move faster and therefore the viscous retarding forces will be larger. Similarly, at lower temperatures the

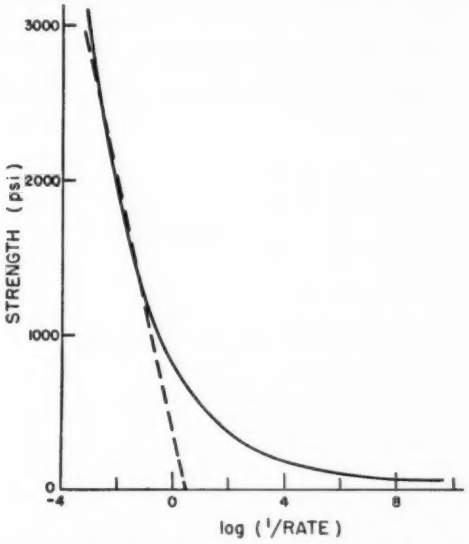

FIG. 10.—Dependence of tensile strength of SBR upon the strain rate[11]. The rate is given in sec^{-1}.

viscous forces will be larger. One would intuitively guess that at some rate of test the energy expended by the testing machine in overcoming these viscous forces will become comparable to the elastic energy which it furnishes to the rubber. At this and higher strain rates, the elongation forces will be considerably increased and the rubber will show a higher tensile strength.

These ideas may be expressed in mathematical terms. Actual calculations have been made for small to moderate strain rates[12] and the expected behavior is found. It is also found that a temperature-time superposition should be valid. In simplest terms, this means that an increase in strain rate would change the tensile strength in the same way as a decrease in temperature. Unfortunately, the theory breaks down at higher strain rates because of the mathematical approximations made.

At very high test rates or at temperatures approaching the glass temperature, a somewhat different way of looking at the molecular processes proves convenient. Under these conditions the network chains are far from being fully extended at the instant of break. The fracture is brittle in nature and is much like one would expect for a glassy plastic. Referring to Figure 11 it is seen that in a slow test near break the chains traverse a given cross section of the sample only once. They have had time to become extended. During a fast test, however, the chains are still rather coiled and traverse the sample cross section several times. Since there are several times more bonds holding the load across a given cross section in the fast test than in the slow test, the strength in a fast test should be much larger than in a slow test. This reasoning can be expressed mathematically and a quantitative result obtained for the tensile strength[13]. It predicts that the tensile strength at high test rates should rise nearly linearly with the logarithm of the test rate. Since the chains will not have extended far enough in such a test for the crosslinks to be of much importance, the reasoning should be the same for all polymers. In fact, the tensile strength of such a material as molten polystyrene shows much the same behavior as rubber under fast tests. The broken line in Figure 10 shows the slope of the tensile strength curve for polystyrene[13] and it is noticed that the behavior is essentially the same as that for SBR.

FIG. 11.—A diagram showing typical network chain configurations under (a) a slow tensile test and (b) a fast test at the instant just before fracture.

The above lines of thought indicate clearly that tensile strength at a fixed temperature is intimately connected with the glass temperature of the rubber. For example, if tests are carried out at room temperature, the tensile strength of a rubber having $T_g = -60°$ C should be much lower than for a similar rubber having $T_g = -20°$ C. In the first case the frictional forces experienced by the network chains will be very low and all ordinary test rates will be slow enough for the chains to elongate readily as the test proceeds. In the second case, the frictional forces are large and the chains will respond only very sluggishly to the applied force. Consequently, the usual rates of test will be too fast for the chains to elongate as rapidly as the test requires. This expected relation between tensile strength and glass temperature was first pointed out by Boyer[14] and also by Borders and Juve[15].

VIII. THE EFFECTS OF FLAWS

Tensile strength measurements are notoriously irreproducible. This fact is the result of the impossibility of making a perfect test sample. Flaws will always be present in any specimen used in a tensile test. These flaws may range from foreign inclusions to density fluctuations. An absolutely pure rubber which had been perfectly molded so as to avoid surface flaws would still possess flaws due to unavoidable statistical errors during the sample preparation. These latter flaws would be in the form of microscopic fluctuations in density, filler con-

centration and crosslink density. It is therefore true that a perfect test sample will never be obtained.

The effects of flaws on the measured strength are very complex. However, certain broad conclusions can be made. Much work has been done to determine what size samples and how many samples should be tested in order to obtain the best estimate of tensile strength[16,17]. There appears to be no general agreement on this point. One must make a compromise in order to obtain reasonable accuracy without excessive labor. The various compromises suggested in the literature agree that several tests should be run on each material but there is considersble difference of opinion as to how the measurements should be made and how the strength should be obtained from these results[17].

In spite of these facts, the following generalization may be made. If the sample size is very small, the chance of finding a large foreign inclusion in the specimen also will be small[16]. The same would be true for other types of flaws which occur rarely in the test material. One would therefor infer that the observed tensile strength should increase as the sample size decreases. This appears to be true in certain cases at least[16]. However it is unlikely that ordinary test samples could be made small enough to eliminate the effects of more numerous microscopic flaws.

IX. SUMMARY

In summary, it is probably true to say that the basic mechanisms responsible for the tensile strength of rubbers are now mostly known. Some disagreement exists concerning the exact role played by crystallinity and filler action. Opinions concerning the way in which the fracture propagates through the sample also differ. It is clear that all the present theories concerning tensile strength are inadequate in many ways. Although the basic ideas involved may be quite correct, much refinement in these theories is still needed. They are only rather crude first approximations to a fully successful theory of tensile strength. It is hoped that this review has been successful in pointing out the successes and failures of current theories so that improvements may be made in them.

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FINE PARTICLE REINFORCING SILICAS AND SILICATES IN ELASTOMERS

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I. INTRODUCTION

Reinforcement has been described[1] as "the enhancement of one or more properties of an elastomer by the incorporation of some ingredient thus making it more suitable for a given application". This definition gives an excellent qualitative description of the reinforcement of an elastomer, but lacks the quantitative aspects necessary to prescribe specifications for materials to be included in the present review on reinforcing siliceous fillers.

The scope of the present review will therefore be defined in terms of the properties of the siliceous fillers rather than in terms of the degree of enhancement of one or many elastomer properties. Experience has shown that substantial improvement in the physical properties of vulcanizates generally cannot be expected from siliceous fillers greater than 50 millimicrons in number average particle size, or less than 50 square meters per gram in specific surface area. These specifications will be used to delineate the silicas and silicates included in the present review, a general outline of which is presented in the following paragraphs:

Description of the silica and silicate fillers is made difficult by lack of established categories for these materials. To aid in their classification, a brief discussion of manufacturing methods is presented. Then, lists of commercially available products are introduced.

Physical and chemical properties of commercially available reinforcing silicas and silicates are presented, based on information in current brochures obtained from manufacturers. Failure by the manufacturer to specify his methods has occasionally diminished the usefulness of published data. For example, the term average particle size is not specific as it does not state which statistical average value is intended. The lengthy treatment given testing methods constitutes a plea to define or specify test methods.

The three properties of primary interest in reinforcing silicas and silicates are the particle size, the chemical nature of the surface, and the state of aggregation. A comprehensive discussion of the chemical nature of the surface is prohibitive because of the wide scope of the topic. Nevertheless, a quick survey was made of this subject with the objective of presenting adequate information to allow an interpretation of the behavior of the fillers in elastomers. The groups encountered are principally siloxane (Si—O—Si), silanol (SiOH), and reaction products of the latter with various hydrous oxides. Attention is focused on silanol groups. Their dehydration and rehydration, their chemical reactivity, and their propensity for hydrogen bonding are considered briefly to aid in understanding interactions of the fillers with elastomers and with curatives.

The most comprehensive portion of this review deals with the reinforcement of elastomers with the silica and silicate fillers. Experience has shown that certain physical tests conveniently performed in the laboratory, such as tensile strength and modulus, reflect a measure of the performance to be expected

from a vulcanizate in service. In turn, these test results reflect changes in spatial structure of the vulcanizate caused by the presence of the filler and by its influence on the vulcanization system. A description is given of the effect of fine particle silicas and silicates on physical properties in elastomer systems, and an interpretation of the effect on network structures is presented. Some new data are shown to clarify some of the concepts of the literature.

By coating fine particle silicas with organic materials, the silicas may become endowed with some of the surface characteristics of carbon blacks. Progress which has been reported in translating silica surface modifications into vulcanizate improvements is discussed.

To treat adequately the practical compounding of silicas and silicates in elastomers is not possible in the present review because of space limitations. Nevertheless, a brief resumé of some of the principles of practical compounding of these fillers is presented.

II. TYPES OF SILICAS AND SILICATES

In the present article, considerable restriction is attached to the term reinforcing filler. Materials greater than 50 millimicrons in number average particle diameter or less than 50 m^2/g in specific surface area are not regarded as reinforcing. Since no naturally occurring silicas or silicates, without modification, fall within these restrictions, such naturally occurring materials as clays or diatomaceous earths are not considered in this review. The only restriction intended for minimum particle size (or maximum surface area) is that the filler be composed of discrete particles: these particles may be aggregated, but must not form a continuum, as in a gel.

For the purposes of the present article, the silicas and silicates will be classified as:

(1) Hydrated
(2) Anhydrous
(3) Aerogel

The largest volume and lowest cost reinforcing siliceous fillers are the hydrated fillers. Hydrated silicas and silicates will be arbitrarily defined as those containing more than 3.5 per cent bound water, and anhydrous fillers as those containing less than 3.5 per cent bound water. Bound water, as will be described in greater detail in Section IV—B, 3, is the ignition loss minus the 105° C weight loss, correction being made for components other than water volatile between 105° C and the ignition temperature.

An aerogel is defined here on the basis of its method of manufacture, to be described in Section III—D, irrespective of its water content. Although the amount of volatile matter found on heating aerogels between 105° C and the ignition temperature may exceed 3.5 per cent, the composition of the volatile matter is largely organic, and the weight loss which is determined for this temperature interval cannot be regarded as all bound water. In fact, the behavior of an aerogel in an elastomer is generally more like that of an anhydrous filler than that of a hydrated filler. Since the only commercial aerogels are the Santocel family, the aerogel category should cause no confusion.

A detailed classification for both black and nonblack fillers has been presented by Endter and Westlinning[2]. Here the process of manufacture is designated by the codes:

PP: pyrogenic process (leads to the formation of solid from molecular dispersion in the gas phase)
TP: thermal process (thermal treatment of solid)
WP: wet process (as, precipitation from aqueous solutions)
MN: modified natural product (as, coated clays)
N: natural products, as clays

Endter and Westlinning did not use the code M for modified. This should have been included to accommodate coated synthetic products. For example, the designation MWP could then be used for a coated wet process filler.

Chemical composition is described by nonstoichiometric representations. Chemical symbols of the main components are separated by a slanted line, as Al/SiO_2; Ca/SiO_2.

Reinforcing capacity is represented by the symbols:

LR: low reinforcing
MR: medium reinforcing
HR: high reinforcing
SR: super reinforcing
ER: extremely reinforcing

Two samples from the article of Endter and Westlinning should suffice to show how they intended that the classification system be used:

Aerosil	PP-SiO_2-ER
Calsil	WP-Ca/SiO_2-MR

It is immediately seen that a definition of degree of reinforcing capacity is required for inorganic fillers before the symbols can be applied to them. For carbon blacks, designations such as HAF (high abrasion furnace), SRF (semi-reinforcing furnace), etc., have been established by usage. However, the variety and volume of carbon black types are numerous, and these types have more or less definite and specialized functions. Manufacturers of siliceous reinforcing agents have usually tended to produce "all-purpose" reinforcing materials in order to maintain economic production levels. Although in practice classifying designations are not applied to inorganic reinforcing agents at present, as their number increases it may become very useful to characterize them by a detailed description or code such as that of Endter and Westlinning.

III. MANUFACTURING METHODS

A. GENERAL

To facilitate an understanding of subsequent discussion of silica and silicate fillers, it would be desirable to present a brief outline of their methods of preparation. Unfortunately, the production details employed by the various manufacturers have been revealed in but few cases, and an analysis of the patent literature would be far too cumbersome for consideration here. However, a brief review of the general procedures by which silica and silicate fillers are produced should help to categorize these materials. A short historical treatment is also presented to aid in referring to the literature.

B. HYDRATED SILICAS AND SILICATES

The preparation of a hydrated silica by acidification of a soluble (alkali) silicate is shown schematically in Figure 1. A typical reaction employing hydrochloric acid could be written:

$$(Na_2O \cdot 3.3SiO_2)aq. + 2(HCl)aq. \longrightarrow 2NaCl + 3.3SiO_2 \cdot hydrate + xH_2O$$

It is well known that one possible product of acidification of sodium silicate is silica gel. Rubber technology recognizes that silica gel is not a reinforcing filler. The preparation of a reinforcing silica by acidification of an alkali silicate is accomplished by careful control of precipitation conditions to produce amorphous discrete particles. The precipitates are recovered and dried as products flocculated to varying degrees, as can be deduced from Figure 4, the electron micrograph of Hi-Sil 233. The first commercial hydrated silica was introduced in 1948 as Hi-Sil, by the Columbia Chemical Division of the Pittsburgh Plate Glass Co., predecessor of the Columbia-Southern Chemical Corporation[3]. Hi-Sil, later known as Hi-Sil 101, was succeeded by Hi-Sil C, later known as Hi-Sil 202. The production of Hi-Sil 101 and Hi-Sil 202 have been discontinued in favor of the present improved product, Hi-Sil 233.

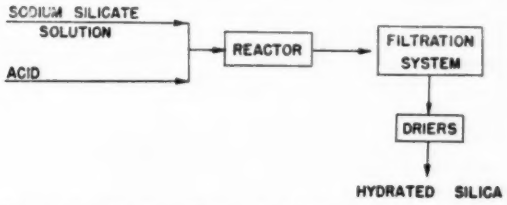


FIG. 1.—Flowsheet for production of reinforcing silica by wet methods.

Precipitation from sodium silicate can be effected by reactants other than acids. For example, using calcium chloride instead of an acid in the flow-sheet of Figure 1 would produce a calcium silicate. The latter process, conducted with minute attention to producing proper particle size and surface characteristics, yields reinforcing pigments such as Silene EF. The general appearance of Silene EF resembles that of hydrated silica pigments, as seen in Figure 5. The first commercial hydrated reinforcing silicate manufactured was Silene, introduced in 1939 by the Columbia Chemical Division of the Pittsburgh Plate Glass Co. With the advent of large scale production of GR-S, it was found that a calcium silicate of finer particle size than that of Silene was desirable for synthetic rubber. Thus Silene was succeeded by Silene EF.

The synthesis of other hydrated silicates by wet procedures is obvious, e.g., reaction of sodium silicate with aluminum salts would produce aluminosilicates. Insoluble silicates may be acidified with acids or acidic salts to produce hydrated fillers. Thus, Allen[4] acidified calcium silicate to produce a hydrated silica. Frantex was the first commercial representative of a modified clay, being introduced into France in 1949 as Frantex B by Franterre, S.A.

Mention should be made of some particularly interesting coated hydrated silica products formerly made by duPont. Two reaction products of fine particle silicas with alcohols which are prominent in the literature are: GS

Hydrophobic Silica 199S and Valron Estersil. The latter was introduced in 1954. Both products have been withdrawn from the market by du Pont.

C. ANHYDROUS SILICAS AND SILICATES

The first important commercial process for producing anhydrous silica for reinforcing rubber was developed by Degussa (Deutsche Gold- und Silber-Scheideanstalt vormals Roessler) in 1940, based on the work of Dr. Harry Kloepfer at Rheinfelden. This process, shown schematically in Figure 2, as presently practiced, reacts silicon tetrachloride, hydrogen, and oxygen at 1850–2000° F to produce anhydrous silica plus hydrogen chloride. This anhydrous silica was first called K-3, and is now designated as Aerosil. Production of this material in the United States under license from Degussa was started in 1953 by Dow-Corning[5] as D. C. Fine Silica, primarily for internal captive consumption in Dow-Corning silicone elastomer masterbatches. It has also been made in the United States since 1958 as Cab-O-Sil by Godfrey L. Cabot, Inc., under license from Degussa[6]. Figure 6 shows an electron micrograph of Cab-O-Sil.

The first commercial reinforcing anhydrous silica manufactured in the United States was Linde Silica[7]. This product was made by burning chloro-

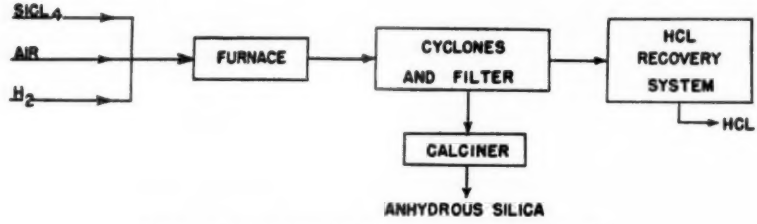


FIG. 2.—Flowsheet for vapor phase production of reinforcing silica.

silanes generated from ferro-silicon. Linde Silica remained on the market for only about a year, when the entry of a low priced hydrated silica filler made the market unattractive for Linde Silica at that time.

A similar product, "white carbon black", announced by the B. F. Goodrich Co. in 1946, was made by burning ethyl silicate by a process analogous to the channel black process. This material, also designated Fumed Silica, has not become commercial.

Fransil is a commercial anhydrous silica filler manufactured in France by Fransol using an electrothermal procedure[8]. It is of interest that an electrothermal process developed by the B. F. Goodrich Co. heated silica and coke in an arc furnace at about 2500° C to produce Monox, a silicon monoxide. Monox is not on the market at present.

The only commercial anhydrous silicate reinforcing filler is Franteg C, a magnesium silicate manufactured by Franterre, S.A., using an electrothermal process.

D. AEROGEL

Aerogel[9] is made by replacing the water in a silica gel with an organic liquid such as alcohol to form an organogel, heating the organogel in an autoclave above the critical temperature of the organic liquid so that no meniscus exists

between liquid and gas phases, and then venting the autoclave. This technique removes the liquid phase without collapsing the gel, since compressive forces due to the surface tension of the liquid-gas interface are absent. A schematic representation of the process is given in Figure 3. The resulting aerogel is typified by the Santocels, which have been marketed by Monsanto since 1947.

The name Aerogel implies a gel structure. Actually, the product has considerable particulate structure, as can be seen by a comparison of its electron micrograph, Figure 7, with that of an anhydrous silica, Figure 6, and of a hydrated silica, Figure 4. Comparison of Figures 4–7 with Figure 8, which is an electron micrograph of Philblack O, shows that these materials have con-

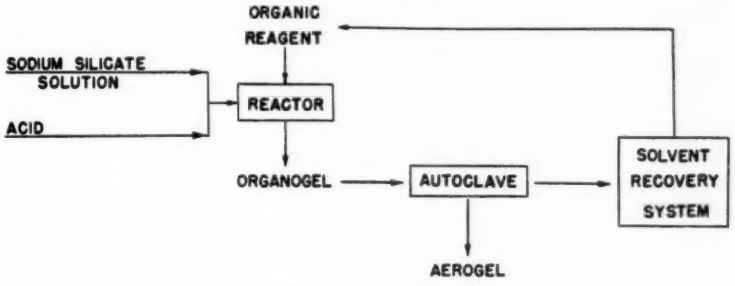


FIG. 3.—Flowsheet for production of aerogel.

siderable similarity. By contrast, a poorly reinforcing material such as Thermax is far different in appearance, as is evident in Figure 9.

IV. PROPERTIES OF FINE PARTICLE SIZED SILICAS AND SILICATES

A. COMMERCIAL PRODUCTS

The reinforcing silicas and silicates currently available commercially are listed in Table I.

The information found in Tables I–V was obtained by direct inquiry to manufacturers, and it was not intended to include jobbers in Table I unless they distributed the product under their own trade mark.

No representative product from the Soviet Union has been included in Table I, although Yashunskaya and Gol'dman[10] report that manufacture of "white soot" involving carbonation of sodium silicate by the method of Subbotin and Lyk'yanchikov[11] has been adopted in the Soviet Union on an industrial scale to give a white powder of specific gravity 2.1–2.2 and particle size of 15–20 millimicrons. Only limited information has been obtained as a result of correspondence directed to Russian sources regarding silicas in volume production.

It will be noted that most of the silicas and silicates of Table I are manufactured outside of the United States. Production figures are not available, but it is believed that production of reinforcing silicas and silicates in the United States is several times that of the rest of the world. Indications are that the production volume of several European manufacturers may be less than ten tons per year. Unfortunately, no estimate of the total volume production is known.

TABLE I

TRADE NAMES OF COMMERCIALLY AVAILABLE REINFORCING SILICAS AND SILICATES

Trade name	Manufacturer	Address
Hydrated silicas		
Durosil, Durosil F	Füllstoff-Gesellschaft Marquart/Wesseling mbH	Wesseling/Rhein, Germany
Hi-Sil 233, X303	Columbia-Southern Chemical Corporation	Pittsburgh 22, Pa., USA
Hoesch KS 160, KS 300	Chemische Fabrik Hoesch K.-G.	Düren, Rhld, Germany
Levilite	Cie. de Saint-Gobain	Paris, France
Manosil VN-3	This is Marquart/Wesseling's Ultrasil VN-3 marketed by Hardman and Holden	Manchester, England
Mikro-Sil A, B	Sawamura Zinc Mfg. Co.	Osaka, Japan
Mikrosil	Gebrüder Giulini GmbH Chemische Fabrik	Ludwigshafen, Germany
Nisil F, G	Nissan Chemical Industries	Tokyo, Japan
Silcafill C	Farbenfabriken Bayer, A.-G.	Leverkusen, Germany
SiFlox	Chemische Fabriken Oker und Braunschweig A.-G.	Oker/Harz, Germany
Sillitin	Franz Hoffman & Sohne Chemische Fabrik	Neuburg, Germany
Silmos	Shiraishi Calcium Kaisha, Ltd.	Kitahama, Higashi-Ka, Osaka, Japan
Sil-Stone	Stoner Rubber Co.	Anaheim, Cal., USA
Ultrasil VN-3	Füllstoff-Gesellschaft Marquart/Wesseling mbH	Wesseling/Rhein, Germany
Vulkasil C, S	Farbenfabriken Bayer, A.-G.	Leverkusen, Germany
Anhydrous silicas		
Aerosil	Degussa	Frankfurt (Main), Germany
Cab-O-Sil	Godfrey L. Cabot, Inc.	Boston 10, Mass., USA
D-C Fine Silica	Dow Corning Corp.	Midland, Michigan, USA
Fransil 251	Fransol	Paris, France
Franteg	Fransol	Paris, France
Aerogil		
Santocel C	Monsanto Chemical Co.	St. Louis, Mo., USA
Hydrated silicates		
Alu-Levilite	Cie. de Saint-Gobain	Paris, France
Alusil	Joseph Crosfield & Sons, Ltd.	Warrington, Lancs., England
Anchor Calcium Silicate	Distributed by Anchor Chemical Co., Ltd.	Clayton, Manchester, England
Calcium Silikat 180	Chemische Fabrik Hoesch, K.-G.	Düren, Rhld, Germany
Calsil	Füllstoff-Gesellschaft Marquart/Wesseling mbH	Wesseling/Rhein, Germany
Calsil AX Calcium Silicate	Salamon & Co., Ltd. Not sold direct. Distributed by Wilfrid Smith, Ltd.	Rainham, Essex, England
Fortafil A70	Imperial Chemical Industries, Ltd.	London, S.W. 1, England
Frantex B and B2	Franterre, S.A.	Paris, France
Manosil AS-7	This is Marquart/Wesseling's Silteg AS-7 marketed by Hardman and Holden	Manchester, England
Microcal	Joseph Crosfield & Sons, Ltd.	Warrington, Lancs., England
NeoFrantex	Franterre, S.A.	Paris, France

TABLE I—(*Continued*)

Trade name	Manufacturer	Address
Silene EF	Columbia-Southern Chemical Corporation	Pittsburgh 22, Pa., USA
Silica Grade A and M	Shearman & Co., Ltd.	Coffinswell, Newton Abbot, Devon, England
Silol	Wilfrid Smith, Ltd.	London, England
Silmos A	Shiraishi Calcium Kaisha, Ltd.	Kitahama, Higashi-Ku, Osaka, Japan
Silteg AS-7	Füllstoff-Gesellschaft Marquart/Wesseling mbH	Wesseling/Rhein, Germany
Tufknit CS	Durham Chemicals, Ltd.	Birtley, County Durham, England
Vulkasil K	Farbenfabriken Bayer, A.-G.	Leverkusen, Germany
Witco Calcium Silicate	Distributed by Witco Chemical Co., Ltd.	London, England
Zeolex 23	J. M. Huber Corp.	New York 17, N.Y., USA
Anhydrous silicate: Franteg C	Franterre, S.A.	Paris, France

B. CHEMICAL PROPERTIES OF COMMERCIAL PRODUCTS

1. *Tables.*—The chemical properties of commercially available reinforcing silicas and silicates are listed in Tables II and III, respectively. Data for these tables were acquired by direct correspondence with the manufacturers, and presumably represent the most recent information available on the products. Occasionally, data for this type of product contradict earlier published values. Manufacturers frequently employ lenient specifications for chemical composition. Moreover, since many of these products had not enjoyed a large volume sales, manufacturers have at times made significant changes in chemical and/or physical properties without changing the product designation. It should be mentioned that very little variation in composition is to be expected for pyrogenic silicas.

2. *Elemental analysis.*—Analysis for the various elements present in silicas and silicates normally is conducted by standard methods of mineral analysis. Metallic elements are reported as their oxides in Tables II and III. Water soluble components such as chloride ion may be determined directly in the water extract. Insoluble constituents are generally determined by fusion methods. The silica or silicate is fused with an alkaline material such as sodium carbonate, the fused mass is digested in water, and the desired component is determined by conventional procedures.

Inspection of Tables II and III shows the anydrous silicas to be high in silica content, generally over 97 per cent on an as-is basis. Silicates used in rubber are generally those of sodium-aluminum, aluminum, calcium, or magnesium. It is often not specified whether the analysis is on a dry or an as-is basis, although simple addition of the components to total 100 per cent will show whether the water was included.

3. *Weight loss on heating.*—Weight loss on heating is a very important characteristic of the silicas and silicates. The common temperature employed for determining "free water" is 105° C, although 110° C is sometimes used. Time of heating may be overnight, although a shorter time may be employed, especially if vacuum is used. This "free water" content of the filler is the adsorbed water which is more or less in equilibrium with the atmosphere at the time of test, and generally under unspecified atmospheric conditions. It presumably represents an average water content which the buyer will find in the product

TABLE II

CHEMICAL PROPERTIES OF COMMERCIALLY AVAILABLE REINFORCING SILICAS*

Trade name	Analysis, % by weight								
		Weight loss							
	SiO_2	105° C	Ignition	CaO	Al_2O_3	Fe_2O_3	Na_2O	pH	Miscellaneous
Aerosil	>99.8[a]	<3	—	—	<0.03	<0.003	—	3.6–4.2	TiO_2<0.06%
Aerosil 2491	>99.8[a]	<3	—	—	<0.03	<0.003	—	3.6–4.2	TiO_2<0.06%
Aerosil 2491/380	>99.8[a]	<3	—	—	<0.03	<0.003	—	3.6–4.2	TiO_2<0.06%
Aerosil "O"	>99.8[a]	<3	—	—	<0.01	<0.001	—	3.6–4.2	TiO_2<0.03%
Aerosil Al 0111/200	>98.3[a]	<3	—	—	0.3–1.5	<0.003	—	3.6–4.2	TiO_2<0.06%
Cab-O-Sil	99.0–99.7[a]	0.2–1.5	0.2–1.0	0.00	—	—	—	3.5–4.2	MgO=0.00% $Fe_2O_3+Al_2O_3$=0.01%
D C Fine Silica	—	—	—	—	—	—	—	—	—
Durosil	83–84	—	11–12	—	—	0.3	2	7	Cl<1%, MnO<0.001%, CuO<0.00025%
Fransil 251	98.5–99	1	1[a]	0.1	0.7	0.2	—	7–7.5	TiO_2-traces
Franteg[b]	—	—	—	—	—	—	—	—	—
Hi-Sil 233	87	5	10	0.5	0.6	0.2 max	—	7.0	NaCl=1%
Hi-Sil X303	88	4–5	10	—	—	—	—	4.5	NaCl=0.04%, Na_2SO_4=0.04%
Hoesch KS160	88	8	10	—	—	—	—	10	Alkali=2%
Hoesch KS300	90	5–6	8	—	—	—	—	7.0	$Al_2O_3+CaO+MgO+Na_2O$=1%
Levilite	98.96	14.6	—	0.17	0.38	—	—	—	—
Manosil VN 3	84–86	5–7	12–14	—	—	0.3 max	—	6–7	—
Mikro-Sil A	—	—	—	—	—	—	—	10.8–11.0	—
Mikro-Sil B	85	—	14[c]	<0.1	—	—	0.3	10.8–11.0	$Fe_2O_3+Al_2O_3$<0.3%
Nisil F	85	14	—	—	—	—	—	7.0–7.2	$MgCO_3$=1%
Nisil G	85	10	6	—	—	—	—	6.5–7.0	$MgCO_3$=1%
Santocel C	90.0–91.5	—	4–5[d]	—	—	—	—	3.8	Na_2SO_4=2–3%

[a] Calculated on water-free basis.
[b] A cheaper off-white variety of Fransil.
[c] Ignition loss at 850° C.
[d] Designated as "volatile".
* As reported by source.

TABLE II—(*Continued*)

Trade name	Analysis, % by weight								
		Weight loss							
	SiO_2	105° C	Ignition	CaO	Al_2O_3	Fe_2O_3	Na_2O	pH	Miscellaneous
SiFlox	88–89	—	10–12	—	—	—	—	7.8–8.3	$Fe_2O_3+Al_2O_3$ ≤0.5%, CaO+MgO ≤0.1%, H_2O soluble = 1.5–1.9%
Sillitin	—	—	—	—	—	—	—	—	—
Silmos	92.42	5.0	7.01	0.05	0.31	0.19	—	8.2	—
Sil-Stone[a]	—	—	—	—	—	—	—	—	—
Ultrasil VN3	86–87	5	11–12	—	—	0.04	—	6	MnO < 0.0001%, CaO < 0.0001%
Vulkasil C	82	5	8	3	—	—	—	—	Cl < 1.0%
Vulkasil S	—	—	—	—	—	—	—	—	—

[a] Sil-Stone is Hi-Sil 233 coated with Linde Modifier 3 (LM-3) silicone oil.

TABLE III

CHEMICAL PROPERTIES OF COMMERCIALLY AVAILABLE REINFORCING SILICATES*

Trade name	Analysis, % by weight							Miscellaneous
					Weight loss			
	SiO_2	CaO	Al_2O_3	Na_2O	105° C	Ignition	pH	
Alu-Levilite	78.8	0.97	7.13	—	12.5	—	—	—
Alusil 165	—	—	—	—	14.0[a]	18.0	9.0	Ratio SiO_2/Al_2O_3 = 7.9/1 W/W Sulfate as SO_4 + Chloride as Cl = 3.0%
Alusil 215	—	—	—	—	12.0[a]	15.0	10.0	—
Anchor Calcium Silicate	60	16	—	—	3	17.5	10	Water solubles = 4%
Calcium Silikat 180	—	—	—	—	—	—	—	—
Calsil	69–70	10–11	—	2.3	—	15	10	Cl < 1%, MnO = traces, CuO < 0.0001%
Calsil AX Calcium Silicate	64.91	18.5	—	—	6.5	16.6	10	TiO_2 < 5 ppm., MnO < 1 ppm.
Fortafil A 70	—	—	—	—	—	—	9	—
Franteg C	88–90	trace	0.5–0.7	—	0.8–1.0	1.5	6	MgO = 8–9%, C = 0.6–0.9%, Fe_2O_3 = 0.3–0.5%
Frantex B[b]	45	1.45	38	—	2.5–3	14.5	8	Fe_2O_3 = 0.8%, K_2O = 0.25%
Manosil AS7	70–74	—	8–8.5	—	5–7	10–12	10–11	Fe_2O_3 = 0.3% max.
Microcal 160	—	—	—	—	13.5[a]	19.0	10.0	A calcium silicate
Microcal 210	—	—	—	—	14.0[a]	18.0	10.5	A calcium silicate
Neo Frantex	—	—	—	—	—	—	—	Similar to Frantex
Silene EF	64	18	0.6	—	5	15	10	Fe_2O_3 = 0.15%, MgO = 0.1% NaCl = 1.5%
Silica Grade A	—	—	—	—	14.0[a]	18.0	9.0	Synthetic aluminum silicate
Silica Grade M	—	—	—	—	13.5[a]	19.0	10.0	Calcium silicate
Silol	—	—	—	—	—	—	—	Aluminum silicate
Silmos A[c]	45.23	18.10	4.51	—	8.0	19.04	9.8	Fe_2O_3 = 0.65
Silteg AS7	69–70	—	7	6–7	6–7	15–16	10	Fe_2O_3 = 0.04%, MnO < 0.0004%, CuO < 0.00015%
Tufknit	59.5	16.0	—	—	—	20.0	10.1	Loss on vacuo = 1.5%, Cu-nil, Mn = nil, Water soluble chlorides = 3.0%
Witco Calcium Silicate	64.91	18.5	—	—	—	16.5	10–11	FeO_2 < 5 ppm, Mn < 1 ppm.
Zeolex 23	65.0	—	12.0	9.8	3–5	9.5	9.5–10.5	

[a] Drying temperature 250° C.
[b] The same analysis is quoted for Frantex B-1 and Frantex B-2. Frantex B-2 has a less ammoniacal odor than Frantex B-1, and gives less darkening in rubber.
[c] A calcium-magnesium silicate.
* As reported by source.

when it reaches his manufacturing establishment. As is seen in Tables II and III, the values range from quite low for anhydrous silicas to almost 15 per cent for some hydrated silicas and silicates.

As may be seen in Table III, 250° C was used for determining the "free water" content of several silicates. Temperatures this high, and higher, are reported in the literature[12] as being necessary to eliminate all absorbed water from clays, such as montmorillonite. This higher temperature is said to be needed to remove hygroscopic or micellar water from the clay surfaces[13]. However, these higher temperatures may remove some combined water from reinforcing type silicas and silicates. It has been found that other standard methods of determining water content, such as the Karl Fischer method, generally agree with the 105–110° C free moisture method, rather than with the higher temperature methods.

Ignition loss includes "free water" and "bound water", as described earlier. The "bound water" is water removed by heating material previously dried at 105° C to elevated temperatures, usually 900°–1100° C or higher for time periods of usually at least one hour. Care must be exercised in interpretation of the results to account for salts volatile at the temperature employed. The source of the "bound water" is condensation of silanol groups on the silica surface, as:

$$2\text{Si—OH} \longrightarrow \text{Si—O—Si} + \text{H}_2\text{O}$$

In general, the anhydrous fillers have quite low free water, bound water, and ignition loss. Bound water as calculated for aerogels or for coated silicas (e.g., Sil-Stone) would include organic matter, and should in fact be designated as volatile matter rather than as bound water.

4. *Hydrogen ion concentration.*—Many manufacturers of silica and silicate powders state that the pH of their products is determined at 4 per cent or at 5 per cent slurry concentration. Others fail to specify the concentrations used. Since silicates often exhibit considerable buffer capacity, the actual slurry concentration of silicates frequently can be varied considerably with but little effect on the pH. However, significant changes of pH may be found for changing silica slurry concentrations. For example, changing a silica slurry concentration from 4 to 5 per cent may easily change the pH value by 0.1 unit. Furthermore, there may be a change in pH with time of standing.

The values reported in Table II for the pH of silicas range from 3.5 to 11.0. The hydrated silicates listed in Table III are all alkaline; only the anhydrous silicate, Franteg C, is acidic.

C. PHYSICAL PROPERTIES OF COMMERCIAL PRODUCTS

1. *Tables.*—The physical properties of commercially available reinforcing silicas and silicates are listed in Tables IV and V. It should be borne in mind that small changes have sometimes been made by manufacturers in the physical properties of their products to effect improvements in their intended applications. When these changes were deemed minor, the product designation sometimes was not changed by the manufacturer.

2. *Surface area.*—The method of surface area determination, when specified by the manufacturer, was always listed as the nitrogen adsorption method of Brunauer, Emmett, and Teller (BET method)[14]. This method assumes that a monolayer of adsorbed gas is formed on the solid prior to the formation of a second layer. A change in the adsorption curve allows the identification of

TABLE IV

PHYSICAL PROPERTIES OF COMMERCIALLY AVAILABLE REINFORCING SILICAS*

Trade name	Surface area m^2/g	Particle dia. $m\mu$	Bulk density, lb/cu ft		Specific gravity	Oil abs.	Refractive index	Miscellaneous
			As-is	Compressed				
Aerosil and Aerosil O	175±25	10–40	2.5	7.8	—	—	1.55	—
Aerosil 2491	300±30	5–20	2.5	—	—	—	1.55	—
Aerosil 2491/380	380±40	3–15	2.5	—	—	—	1.55	—
Aerosil Al 0111/200	200±25	10–40	2.5	—	—	—	1.55	—
Cab-O-Sil	175–200	15–20	2.3–3.5	6.0–6.5	2.1	150	1.55	—
DC Fine Silica	—	—	—	—	—	—	—	—
Durosil	—	20	8.1	15.6[a]	2.1	—	—	Agglomerates ca 200$m\mu$
Fransil 251	—	40	—	—	2.2	—	—	—
Franteg[f]	—	—	—	—	—	—	—	—
Hi-Sil 233	150	22	10	—	1.95	135–165	1.46	—
Hi-Sil X303	160	22	3	—	1.95	145–160	1.445	—
Hoesch KS 160	110	25	10	—	1.95	—	—	—
Hoesch KS 300	180	20	9.4	—	1.95	—	—	—
Levilite	360	7.5	6.9	—	—	—	—	—
Manosil VN3	—	15–20	12.5	16.9[b]	1.95	150–160	1.45	—
Mikro-Sil A	—	—	8	—	1.92	—	1.49	—
Mikro-Sil B	—	—	6.2	—	1.95	—	1.44	—
Nisil F	—	10–50	—	—	1.92	35[c]	—	—
Nisil G	—	50–100	12.5	—	1.85	33.7[c]	—	—
Santocel C	130	300–500[d]	5	—	—	300	1.45–1.46	—
SiFlox	—	10–30	3.1–3.4	—	2.00–2.10	—	—	—
Sillitin	—	—	—	—	—	—	—	—
Silmos	30–40	—	—	—	1.97	—	—	—
Sil-Stone[e]	—	—	—	—	—	—	—	—
Ultrasil VN3	—	16	4.4–5	7.2–8.4[a]	1.9–2.0	—	—	—
Vulkasil C	80	30	6	7.8[a]	1.95	—	—	—
Vulkasil S	150–200[g]	—	—	—	—	—	—	—

[a] Shaken bulk density.
[b] Tapped bulk density.
[c] Diphenyl guanidine absorption.
[d] This value, from Monsanto literature, doubtlessly refers to aggregate size. Ultimate particles are much smaller.
[e] Sil-Stone is Hi-Sil 233 coated with Linde Modifier 3 (LM-3) silicone oil.
[f] A cheaper off-white variety of Fransil.
[g] See Reference 20.
* As reported by source.

TABLE V

PHYSICAL PROPERTIES OF COMMERCIALLY AVAILABLE REINFORCING SILICATES*

Trade name	Surface area m^2/g	Particle dia. mμ	Bulk density, lb/cu ft		Specific gravity	Oil absorp.	Refractive index	Miscellaneous
			As-is	Compressed				
Alu-Levilite	260	10.4	11	—	—	—	—	—
Alusil 165	170	30–50	6.5	—	1.95	180	1.45	Pore volume = 0.28 cc/g. Pore dia. = 70A
Alusil 215	—	30–50	14	—	1.95	110	1.45	—
Anchor Calcium Silicate	—	50	—	—	—	—	—	—
Calcium Silikat 180	—	—	—	—	—	—	—	—
Calsil	—	40	9.4	18.71[a]	2.05	—	—	Agglomerates = 300 mμ
Calsil AX Calcium Silicate	—	<10	7.8	—	1.862	140–160	—	—
Fortafil A 70	105	30	—	—	2.1	—	—	—
Franteg C	—	10–12	7.5–8.7	—	—	—	—	—
Frantex B-1 and B-2	—	10.6	62	—	2.35	—	—	—
Manosil AS 7	—	45–50	10	14[b]	1.95	120–130	1.47	—
Microcal 160	—	30–50	6	—	2.1	140	1.47	—
Microcal 210	—	30–50	10	—	2.0	140	1.45	—
Neo-Frantex	—	—	—	—	2.4	—	—	—
Silene EF	80	30	12	—	2.1	120	1.47	—
Silica Grade A	—	30–50	6.5	—	1.95	180	1.45	—
Silica Grade M	—	30–50	6	—	2.1	140	1.47	—
Silol	—	—	—	—	—	—	—	—
Silmos A	140–160	—	—	—	2.0	—	—	—
Silteg AS 7	—	35	4.4–5	8.1–9.4[a]	1.9–2.0	—	—	—
Tufknit CS	50	—	11	—	2.1	—	1.47	Agglomerates (optical microscope) 1000mμ
Witco Calcium Silicate	—	—	7.8	—	—	150–200	—	—
Zeolex 23	72	20–30	—	—	2.1	123–133	1.55	—

[a] Shaken bulk density.
[b] Tapped bulk density.
* As reported by source.

complete monolayer formation and, from the knowledge of the cross-sectional area of the adsorbed molecules, the surface area of the solid may be calculated. The comparison of particle size as deduced from adsorption measurements with that calculated from electron micrographs will be discussed after the latter method has been described.

It should be mentioned that methods of surface area determination based on adsorption of molecules from solution have been devised, e.g., adsorption of methyl red (paradimethylamino azobenzene orthocarboxylic acid) from benzene solution by the method of Shapiro and Kolthoff[15].

Silicas and silicates of specific surface area less than 50 m^2/g, are generally not regarded to be reinforcing in elastomers. The only material included in the tables with lower surface area was the silica, Silmos at 30–40 m^2/g, which was included to avoid confusion with the silicate Silmos A. Examination of Table VI shows that the surface areas of reinforcing silicas and silicates are generally slightly higher than those of the reinforcing carbon blacks.

3. *Particle diameter.*—Particle diameters in Tables IV and V were presumably all obtained from electron micrographs. Common practice is to measure the diameters of several hundred particles. Although the maximum amount of information is deduced from a particle size distribution curve, it is conven-

TABLE VI

COMPARISON OF PARTICLE DIAMETERS AND SURFACE AREAS OF TYPICAL SILICA AND SILICATE REINFORCING FILLERS WITH THOSE OF TYPICAL CARBON BLACKS

Filler	Particle diameter[a] mμ	Surface area m^2/g
Cab-O-Sil	15–20	175–200
Hi-Sil 233	22	150
Silene EF	30	80
Zeolex 23	20–30	72
Philblack A[b]	38.4	45.8
Philblack O[b]	29.4	79.6
Philblack I[b]	28.6	116.8
Philblack E[b]	17.5	135.1

[a] The statistical average diameter employed not stated.
[b] Reference 19.

ient to express the results in terms of an average diameter such as the number average diameter,

$$d_{av} = \frac{n_1 d_1 + n_2 d_2 + \cdots + n_n d_n}{n_1 + n_2 + \cdots + n_n} = \frac{\Sigma nd}{\Sigma n} \qquad (1)$$

where n_1, n_2, etc., are the numbers of particles having diameters d_1, d_2, etc., respectively. Other mean diameters may be calculated[16], one of the most useful being the mean volume-surface diameter, sometimes called the surface-average diameter,

$$d_s = \frac{\Sigma nd^3}{\Sigma nd^2} \qquad (2)$$

This is the diameter of a particle having a specific surface area equal to the average calculated for all measured particles. Because of the obvious comparison of this diameter with that calculated from BET measurements, the use of this

diameter is quite common of materials for the size encountered in reinforcing fillers.

One other useful diameter is the weight mean diameter:

$$d_w = \frac{\Sigma n d^4}{\Sigma n d^3} \tag{3}$$

Although accepted statistical average diameters have been defined, electron microscopists frequently estimate an average diameter. Usually, the obviously

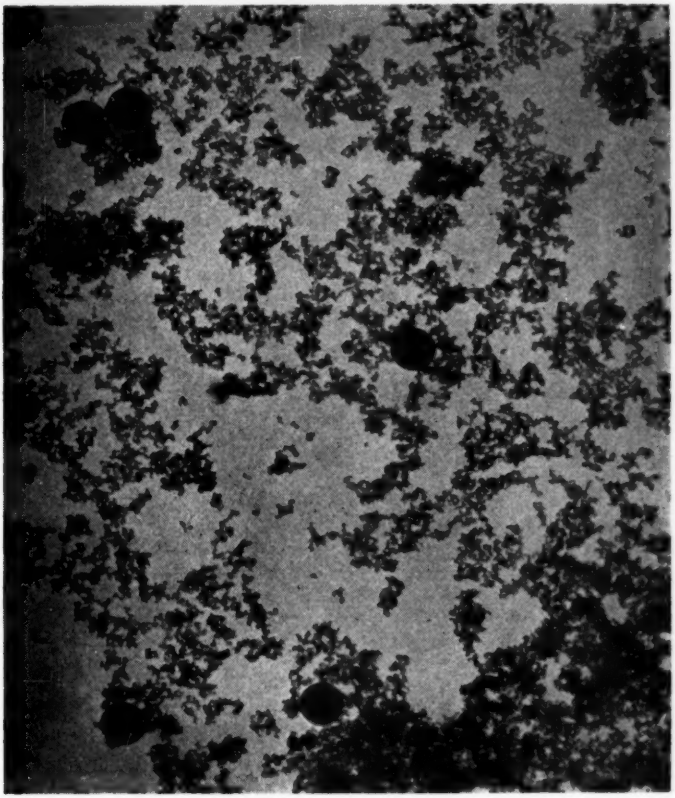


FIG. 4.—Electron micrograph of Hi-Sil 233.

oversize and undersize particles are ignored, a range of the most common particle sizes is estimated, and the average of the range is quoted as the average particle size. It is generally believed that the estimate corresponds most closely to a number average. To make a frequency analysis on routine samples would be prohibitively time consuming, and the practice of estimating particle sizes is

certainly justified. For scientific calculations, however, a well defined average size is necessary.

It is assumed that the particle diameters of Tables IV and V are, for the most part, estimates, number average diameters, or surface average diameters, and usually an estimated diameter. These are generally obtained from electron micrographs of the type shown in Figures 4–9. To aid in particle diameter estimation, an internal standard is used, particularly Dow Latex 580 G, which

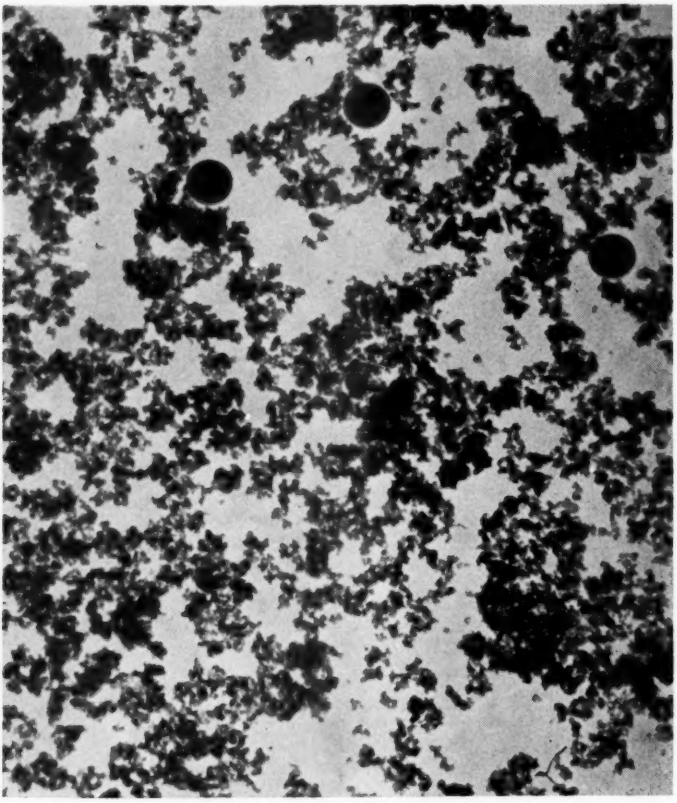


FIG. 5.—Electron micrograph of Silene EF.

is composed of polystyrene spheres which have a uniform diameter of about 2850 A[17]. Watson and Grube[18] have discussed the validity of the 2850 A diameter. These spheres are apparent on the electron micrographs of Figures 4–9.

The particle sizes of the reinforcing silicas and silicates seem to be slightly less than those of reinforcing carbon blacks[20]. This may be illustrated by the brief tabulation of Table VI.

4. *Comparison of surface area and particle diameter.*—As has been stated earlier, the surface-average diameter calculated from electron micrographs should compare with the diameter calculated from BET surface area measurements. Thus, if d_s is the surface average diameter, πd_s^2 is the surface area of a single particle with this diameter. In Tables IV and V, diameters are expressed in millimicrons and specific surface area in m^2/g. Then,

$$\pi d_s^2 \cdot 10^{-18}$$

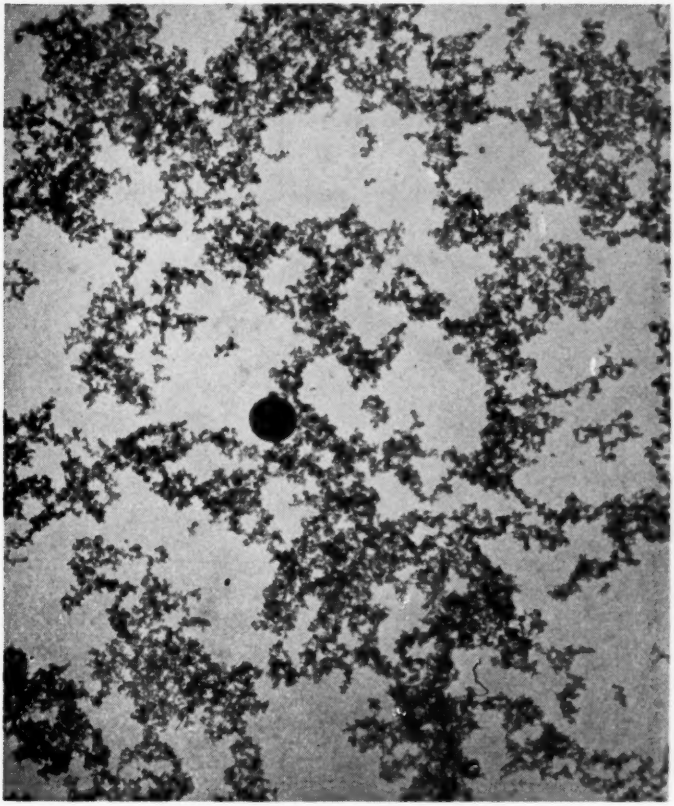


FIG. 6.—Electron micrograph of Cab-O-Sil.

is the surface area of a single particle in sq m. Its volume in cu m is,

$$\tfrac{1}{6}\pi d_s^3 \cdot 10^{-27}$$

Specific gravity, ρ, is expressed in g/cc. Therefore, the weight of the single particle is,

$$\tfrac{1}{6}\pi d_s^3 \cdot 10^{-27} \cdot 10^6 \rho = \tfrac{1}{6}\pi d_s^3 \rho \cdot 10^{-21}\ g$$

Hence, specific surface area is:

$$\frac{\text{Surface area/particle}}{\text{Weight/particle}} = \frac{\pi d_s^2 \cdot 10^{-18}}{\frac{1}{6}\pi d_s^3 \rho \cdot 10^{-21}}$$

$$= \frac{6 \cdot 10^3}{\rho d_s} \text{ m}^2/\text{g} \qquad (4)$$

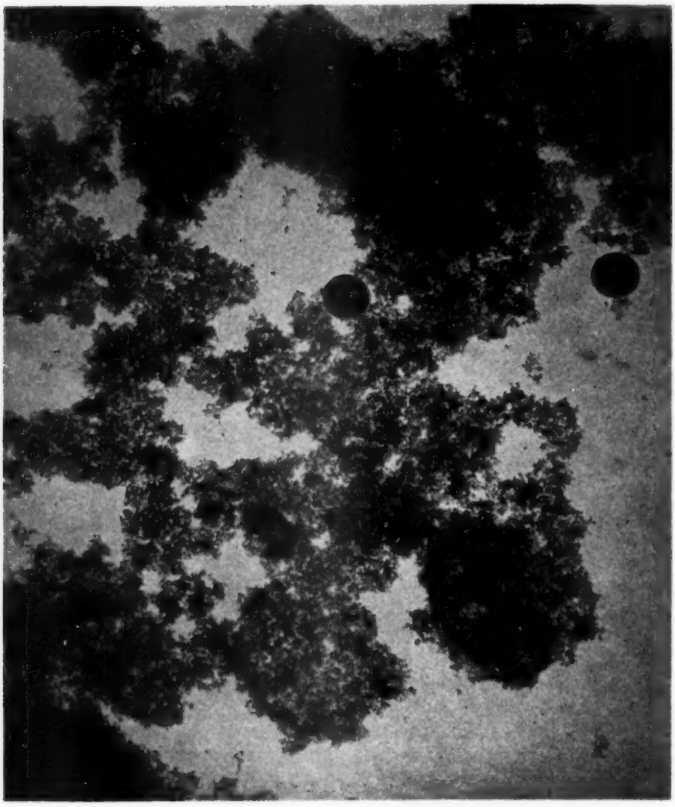


FIG. 7.—Electron micrograph of Santocel ARD.

The preceding expression was derived in some detail since many calculations relative to surfaces employ the above concepts, and an elementary reference may be helpful. In particular, the above derivation may be of assistance in clarifying problems regarding units.

Comparison of particle diameters and specific surface areas in Tables IV and V reveals that considerably more surface area is found by nitrogen adsorption than would have been calculated from electron microscope surface average

particle diameters. The discrepancy is attributed to surface roughness or porosity, or to the presence of interstices in the aggregates. One expression of the discrepancy in surface areas calculated by the two methods is the roughness factor[21]. The reciprocal of this term is referred to as the coalescence or reticulation factor[22], and is the ratio of the surface area calculated from the surface average diameter to that determined by the BET method. This ratio is units for perfectly smooth spheres which are not physically joined, and decreases

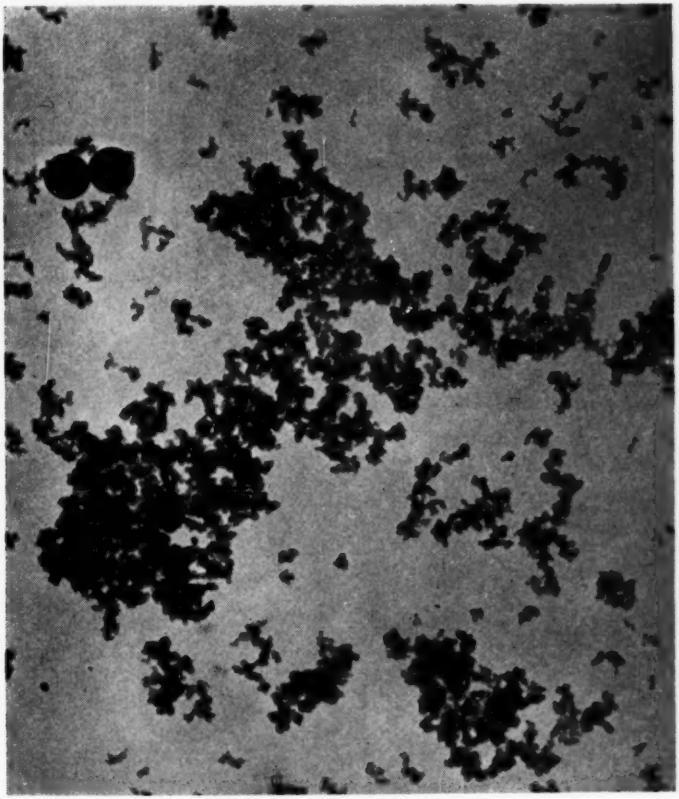


FIG. 8.—Electron micrograph of Philblack O.

with increasing surface irregularities or increases with increasing coalescence of particles within aggregates.

The importance of these considerations to the problem of reinforcement of elastomers is reflected in the fact that the criteria of reinforcing fillers were chosen to be surface area ($\geqslant$ 50 m^2/g) and particle size ($<$ 50 mμ). Furthermore, when surface area is too high, there is adsorption of accelerators which disrupts cure. In general, the higher the surface area of the filler, the greater its adsorbing power. This adsorption may be due in part to the existence of

pores in the individual particles, or even of inter-particle capillaries. In general, the pores are too small to allow elastomer molecules to penetrate, and therefore do not contribute to reinforcement[23].

Voet[23,24] has shown how to calculate pore size distributions down to the 18–40 A diameter range with spherical particles by adsorption methods.

5. *Bulk density and specific gravity.*—Bulk density in Tables IV and V is expressed in lb/cu ft. Manufacturers frequently quoted this value in grams/

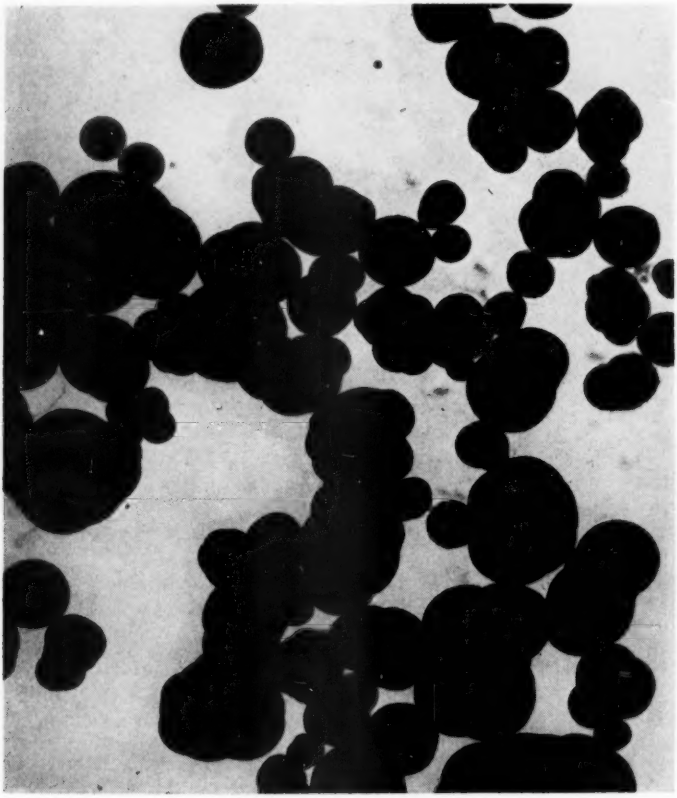


FIG. 9.—Electron micrograph of Thermax MT.

liter or similar units (1 g/l = 0.06243 lb/cu ft). As-is bulk density gives the weight of a given volume of uncompacted material. Manufacturers' information frequently failed to specify the method employed to determine compacted bulk density. When stated, the method given was either tapped or shaken bulk density. For determining tapped bulk density, a container (e.g., a graduate) is tapped a fixed number of times, or until the sample has settled to a constant level. Similar considerations hold for shaken bulk density values.

Some quite low values for bulk density are found for dry process silicas

(Aerosil and Cab-O-Sil) unless the products are compressed. Otherwise, there seem to be no generalizations regarding bulk density which are applicable to the fillers.

The importance of bulk density to reinforcement is not apparent. Frequently, bulk density of a given silica or silicate seems to be primarily a function of the degree or kind of grinding in the absence of compaction. Bulk density seems significant primarily in dusting or storage problems. Low bulk density of silicas and silicates as compared to carbon blacks is disadvantageous to the rubber compounder. Presumably, higher bulk density for these materials could be attained by known compacting techniques.

Specific gravity methods are generally unspecified by the manufacturer. All values quoted fall in the range 1.85–2.4. In the rubber industry, these values allow calculation of volume loading of stocks and, therefore, are of immense practical importance. However, specific gravity appears to play no part in reinforcement per se. Nevertheless, the high specific gravity of these fillers compared to about 1.80 for carbon black is disadvantageous on a volume loading basis.

6. *Oil absorption.*—The oil absorption values of Tables IV and V represent the g of linseed oil required by 100 g of the filler to form a paste. A good description of the procedures used for this test is given by Gardner and Sward[25]. Reproducibility with the method is rather poor when using solids of high surface area. The paste is usually made by rubbing the oil into the solid with a spatula, and the end point is affected by the degree of mechanical manipulation during making of the paste.

In the oil absorption method, it is assumed that the oil may fill spaces between ultimate particles. Thus, the oil absorption values should be related to the state of aggregation of the filler or the openness of packing of the aggregates. Unfortunately, the degree of mechanical manipulation affects the degree of wetting of the particle by the oil. Furthermore, some of the pores in the individual filler particles may fill with oil. These are probably among the reasons that, as yet, no useful correlation between state of aggregation or pore volume and oil absorption has been reported for reinforcing fillers. However, a modification of the test employing water instead of oil has shown some correlation with reinforcing power as shown in Section IV—E. It is interesting to note the high percentage of manufacturers who deemed oil absorption values important enough to report (Tables IV and V).

7. *Refractive index.*—As is seen in Tables IV and V, many manufacturers of reinforcing silica and silicate fillers report a refractive index. The range of values reported, 1.44–1.55, is fairly narrow. The importance of the refractive index values for these fillers is that they fall close to the range found for various elastomers (1.50–1.525)[26,27] and that these fillers are, therefore, often suitable for the preparation of transparent stocks.

D. THE CHEMICAL NATURE OF THE FILLER SURFACE

1. *General.*—To facilitate an understanding of the interactions of silica and silicate fillers with elastomers and with compounding ingredients, a survey is presented of the chemical nature of the silica and silicate surfaces. Since an exhaustive review of the chemical nature of these surfaces is not possible because of space requirements, only a brief consideration of the subject is made, with the objective of providing orientation to those unfamiliar with silica and silicate chemistry.

2. *Spectroscopic studies.*—Although gross properties of surfaces are usually studied, there is information available regarding individual functional groups on the surfaces, primarily from infrared spectroscopy. In the case of hydrated silica surfaces, the silanol group has been identified, and some of its interactions with other molecules have been analyzed.

Among the most revealing of the recent studies of siliceous materials by infrared spectroscopy have been those of McDonald[28,29] and Young[30]. For an anhydrous silica with but few surface silanol groups, or for a hydrated type of silica which has been partially dehydrated, a rather sharp band at 3750 cm^{-1} indicates that the surface hydroxyl groups are relatively homogeneous. As the number of hydroxyl groups on the surface increases, the 3750 cm^{-1} band broadens. This is interpreted as due to hydrogen bonding between adjacent OH groups. Lowering of the band frequency resulting from the adsorption of

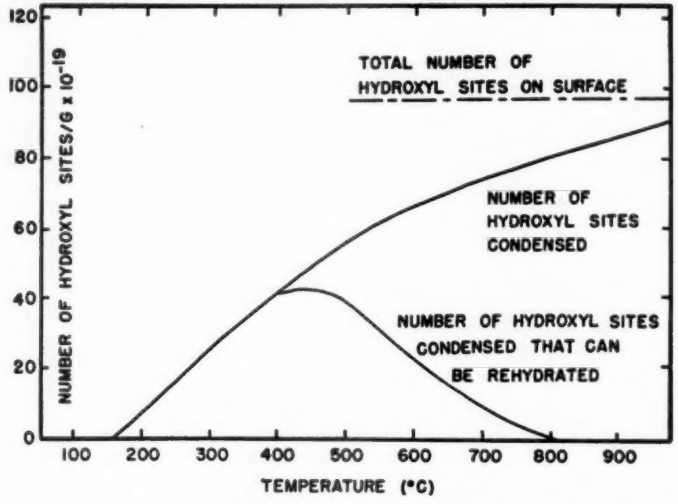


FIG. 10.—Change in surface silanol sites with sample heat treatment (after Young, Reference 30).

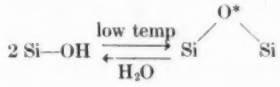
even such nonpolar molecules as nitrogen, oxygen, methane, etc., was interpreted as due to hydrogen bonding.

Infrared spectroscopy thus can be used to demonstrate the presence of individual hydroxyl groups on the silica filler surface, and to show interaction between these hydroxyl groups and other substances. A reasonable interpretation of these interactions appears to exist in the concept of hydrogen bonding.

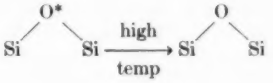
3. *Hydration-dehydration relationships.*—A description of the terms free water and bound water was given in Section IV—B, 3. Bound water was defined as water removed from 105° C dried material by heating at temperatures in the neighborhood of 1000° C and it was said to derive from condensation of silanol groups. Actually, elimination of bound water starts at temperatures much below 1000° C. Thus, if a 105° C dried sample of a hydrated silica is heated at 250° C, there will be some weight loss. The heated sample can be reversibly rehydrated by exposure to water vapor. However, after heating

to 400° C, rehydration of the surface is no longer completely reversible. In fact, the higher the silica is heated, the less will be the water regain of the heated sample upon exposure to water vapor. This may be illustrated by Figure 10, a duplication of a curve obtained by Young[30] for a silica sample which he heated to different temperatures, and then exposed to water vapor.

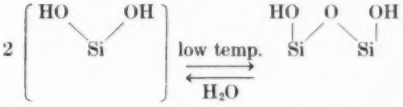
A mechanism advanced by Young[30] to explain the above results assumes that a low temperature dehydration (say, at 250° C) forms strained siloxane bonds as shown, designated by an asterisk:



This strained site can absorb water, but at higher temperatures (above 400° C) a different type of surface bond which cannot absorb water may form as a result of relieving the strain, as:



It is possible that the postulated strain is influenced by close-neighboring silanol sites not yet dehydrated. In fact, close-neighboring silanols might constitute a site which could physically adsorb water and initiate rehydration. This could be illustrated by the mild dehydration of a system of two neighboring silicon atoms, each with two attached hydroxyls, as:



It appears that the surface of anhydrous silicas is composed mainly of siloxane groups. The surface of a hydrated silica may contain principally silanol groups, capable of being dehydrated to siloxane groups by heat. The maximum number of silanol groups that can be accommodated on a spherical surface can be expressed in terms of the relations:

$$x = \frac{22\pi}{6} d^2 \tag{5}$$

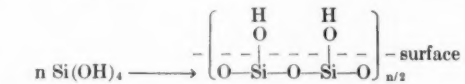
$$y = \frac{\pi}{2} (2.80d)^2 \tag{6}$$

where d is the particle diameter in millimicrons, and x and y are defined by the formula $(SiO_2)_x(H_2O)_y$. A derivation of these equations is presented by Iler[31] assuming that all silanol groupings reside on the particle surface.

4. *Some chemical reactions of silanol groups.*—X-ray studies have revealed the structure of many crystalline silicates. The fundamental unit from which silicates are derived is the SiO_4 tetrahedron, with four oxygen atoms at the

corners of a regular tetrahedron and a silicon atom at the center. Two different SiO_4 groups may share a single oxygen atom. If two oxygen atoms per SiO_4 group are shared with other SiO_4 groups, the structure is a chain. Sharing three atoms per SiO_4 group gives a sheet, and sharing all oxygen atoms gives a three-dimensional network. Generally, the reinforcing silicas and silicates are amorphous, but amorphous materials are still presumably built of microcrystalline units.

Hydrated silicas may be thought of as condensation products of silicic acid:



In the above representation, hydroxyls are present at the surface of the polysilicic acid. Inside the surface, binding is probably predominantly via sharing of SiO_4 groups. Although microcrystalline structures are presumed to be present, the sharing of SiO_4 groups is rather chaotic, and gives an amorphous product. Calcination brings order and therefore crystallinity to these structures.

It is the reactions of the surface hydroxyls or silanol groups which are primarily responsible for the surface chemical properties of the hydrated silicas. A brief mention of the nature of the silicon-oxygen bond may be appropriate. Two references in particular point out π-bond character, which has implications in reinforcement. MacDiarmid[32] stated that the silicon-oxygen bond must possess appreciable π-bond character by inference from surface tension measurements and parachor calculations on disilyl sulfide, $(SiH_3)_2S$. Nuclear magnetic resonance spectra measurements of Allred, Rochow, and Stone[33] showed the silicon-oxygen bond in trimethyl silanol to be relatively highly polar. They concluded that there must be a certain amount of d_π—p_π bonding, involving p electrons from oxygen and vacant 3d electron orbitals in silicon.

The published information on the reactions and reactivity of the silanol group is too vast to survey, and the following discussion is intended to be illustrative rather than comprehensive. It will aid in appreciating literature relating to coated silicas and silicates to review several of the more common chemical reactions of silanol groups. For convenience, reference is made to recent articles on organic derivatives of hydrated silicas and clays by Deuel[34].

The silanol group shows many of the reactions characteristic of alcohols. For example, a silicon-chlorine bond is formed with thionyl chloride as:

$$\text{Si—OH} + \text{SOCl}_2 \longrightarrow \text{Si—Cl} + \text{SO}_2 + \text{HCl}$$

This silicon-chlorine bond participates in expected reactions such as Friedel-Crafts

$$\text{Si—Cl} + \text{C}_6\text{H}_6(\text{AlCl}_3) \longrightarrow \text{Si—C}_6\text{H}_5 + \text{HCl}$$

or Grignard

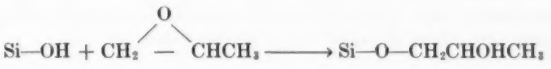
$$\text{Si—Cl} + \text{EtMgI} \longrightarrow \text{Si—Et} + \text{MgICl}$$

or alkoxylation reactions.

The expected reactions of carbonyl chlorides with silanol groups occurs:

$$\text{Si—OH} + \text{ClCOR} \longrightarrow \text{Si—O—COR} + \text{HCl}$$

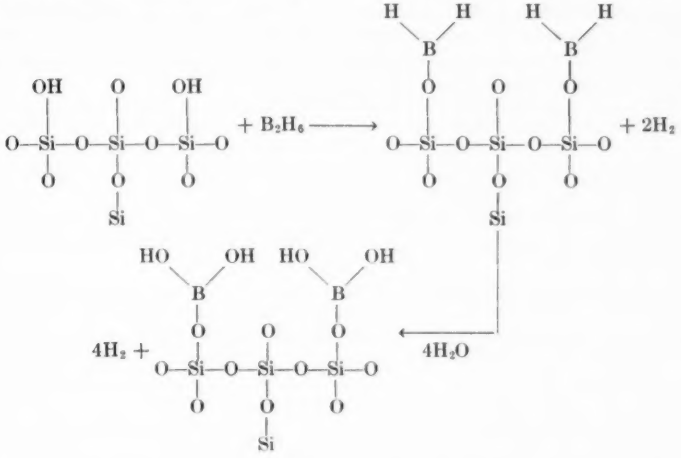
Deuel[34] stated that about 87 per cent of the acid groups on a hydrogen clay are esterified by epoxides, as:



A particularly interesting derivative was the esterified silica ("Estersil") of Iler[35], who reacted a hydrated silica with an alcohol. A portion of the surface silanol groups became esterified, forming an organophilic product. A butanol esterified silica was sold by duPont as Valron, but is no longer available commercially.

Since many of the interactions between hydrated silica fillers and curing ingredients can be interpreted in terms of hydrogen bonding, mention is made of a rather lengthy summary of the complexes between polysilicic acid and polar organic compounds (including polymers such as proteins and cellulose) by Iler[36]. Compounds shown which display hydrogen bonding with polysilicic acids include alcohols, glycols, ketones, amides, and amines. Since curing agents frequently fall into one or several of the latter categories, the possibility of hydrogen bonding between them and polysilicic acids is apparent.

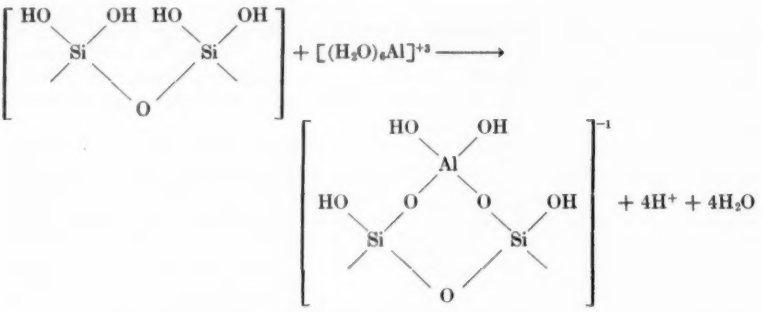
Attention has been focused on the chemical structure of fillers from the point of view of the isopoly acid (contains but a single type of anhydride), polysilicic acid. Heteropoly acid (contains more than one single type of anhydride) structures can, in fact, be regarded quite simply as derivatives of polysilicic acid. This may be illustrated quite simply by citing two cases: the introduction of boron into a polysilicic acid structure without change of coordination number, and the introduction of aluminum with a change of coordination number. Consider the coating of a hydrated silica particle with boron oxides for use as a catalyst, as proposed by Shapiro[37].



The principle of the preparation is that the bound water of oxide gels reacts with diborane. This procedure has been used by Shapiro and Weiss[38] to

determine the bound water in silica gel, and the work is reported to be applicable to silica-alumina gels. Note that when the boron entered the lattice (at the surface), it retained its coordination number of three.

When the surface of a hydrated silica is coated with alumina, the aluminum "ion" fits into the lattice in tetrahedral coordination, as:



Note that the position which normally would be held in the lattice network by a tetravalent silicon is occupied by trivalent aluminum, leaving a negatively charged site at the surface. Structures of this type are represented by the well-known aluminosilicate catalysts, which have been studied at length. Loewenstein[39] has formulated rules for the linking of tetrahedra occupied by silicon and of tetrahedra (and octahedra) occupied by aluminum. These principles must hold whether the gross lattice is crystalline or amorphous.

Any cations present on the heteropoly acid or on the parent isopoly acid, polysilicic acid, may be then regarded as present through ion exchange. The concept of ion exchange is very common for clay materials, and its extension to reinforcing hydrated silicas and aluminosilicates should present no problem. In the simplest case, a hydrated silica when slurried with a salt solution will acquire some bound sodium by the mechanism:

$$\text{Si—OH} + \text{Na}^+ \longrightarrow \text{Si—ONa} + \text{H}^+$$

Verifying this will be a decrease in the pH of the salt solution after addition of the hydrated silica. Reactions similar to the above would be expected between hydrated silicas (polysilicic acids) and other cations. In particular, calcium silicate can be thought of as the product of ion exchange between calcium ion and polysilicic acid.

When discussing the chemical composition of reinforcing hydrated silicas and silicates, attention was directed to the lenient specifications sometimes employed in their manufacture. Ion exchange phenomena are often responsible for variations in product composition. For example, seasonal changes in the composition of wash waters employed in hydrated silica and silicate manufacture might easily cause variations of product composition due to ion exchange. This becomes immediately apparent when one considers that among commercial water softeners are the zeolites, which include both natural and synthetic silicate materials.

The extent to which contamination of fillers can be tolerated depends on

the application. For example, Kunowski and Hofmann[40] reported that the dispersibility of silicate fillers was diminished by the presence of a high content of exchangeable sodium ions on the surface, although the presence of calcium ions counteracted the deleterious action of the sodium. They also report that, because of the poorer dispersibility, the high sodium content fillers gave softer vulcanizates.

E. THE STATE OF AGGREGATION

It is accepted as axiomatic that "structure" influences the ability of a carbon black to reinforce elastomers. By analogy, a similar property in silica and silicate fillers is presumed to play an important role in reinforcement.

No parameters listed in Tables IV and V define state of aggregation. To some extent, the oil absorption values have been interpreted in terms of aggregation, but this approach has been of little value. An apparently equivalent type of test is a water absorption test employed on silicas by Dogadkin, Pechkovskaya and Gol'dman[41]. Here, the quantity of water which is absorbed by a sample on stirring water into it until there is an abrupt change in paste viscosity is defined as moisture absorption capacity or water number. A rather rough correlation was found between moisture absorption of the filler alone and the tensile strength in vulcanizates of several fillers which were classified as active, medium active, or inactive. It is hoped that the moisture absorption capacity or a related test may prove of merit in evaluating silicas (and/or silicates). In another interesting set of experiments, Dogadkin, Pechkovskaya and Gol'dman[41,42] studied the degree of aggregation of colloidal silicic acid in sodium-butadiene rubber. Using the analogy that active carbon blacks capable of reinforcing elastomers form thixotropic mixtures in which the carbon black particles come into contact with each other to a certain degree, giving lattice structures, they believed that chain structures of silicas should be capable of penetration by sodium hydroxide solutions. In the absence of "structure", it was believed that penetration by sodium hydroxide solution would be hindered by more or less thick layers of elastomer between the isolated silica particles. Rubber-elastomer mixtures were calendered to a 0.8–1.0 mm thickness, and samples were refluxed in one per cent sodium hydroxide solution. The latter, penetrating the "structured" silica, dissolved this silica. A lixiviation coefficient was defined as the fraction of the total filler content passing into the alkali solution in ten hours of extraction time. Samples were divided into three groups:

1. Inactive samples, whose lixiviation coefficient was less than 25 per cent.
2. Samples of average activity, whose lixiviation coefficient was 40–50 per cent.
3. Active samples whose lixiviation coefficient reached 70–100 per cent.

Although the paucity of the data precluded a critical evaluation of the usefulness of the method, it seems to be an ingenious way to study "structure" of siliceous fillers in elastomers.

The appearance of the fillers under the electron microscope permits an evaluation of aggregation, although the field is generally too limited to give a representative sample of the aggregates (*cf.* Figures 4–9). Flemmert[43], defining the state of aggregation of fillers in terms of the appearance of the electron micrographs, divided fillers into four different classes described as follows:

Class I. These are compact, irregularly shaped aggregates which are not broken up during mixing into the rubber and which are so compact that rubber can not significantly penetrate the individual aggregates.

Class II. Here, loose irregular aggregates are broken up during mixing into the rubber to give close contact between the primary particles and the rubber.

Class III. These are rod-like aggregates in which the primary particles can come into intimate contact with the rubber even if the aggregates are not broken up to a significant extent. Most of the carbon blacks belong to this class.

Class IV. In this category, primary particles do not become associated into aggregates.

Of necessity, the Flemmert classification is only a rough measure of the degree of aggregation of the filler. Although Flemmert presents electron micrographs of four silicas to illustrate the categories, different ratings may be found for a given filler by different laboratories since the apparent degree of aggregation of a sample may be influenced to a marked extent by the technique of sample preparation for the electron microscope. Furthermore, a single filler may be so heterogeneous that it shows all four classes of aggregation. An electron micrograph study of the siliceous fillers in elastomers might help elucidate the structure problem.

Flemmert[44] attempted to describe the degree of aggregation more precisely by estimating this property to be low, medium, or high. A low degree of aggregation is ascribed to an aggregate having its longest dimension smaller than five times the mean particle diameter. The medium category is used when the ratio of the aggregate's longest diameter to the mean particle diameter is 5–10, and the high degree of aggregation designates that the ratio is greater than 10.

Despite the ambiguities inherent in Flemmert's classifications, they provide a qualititative manner for differentiating between aggregated fillers. Within a given laboratory, and employing standardized techniques of sample preparation, use of the Flemmert classifications would doubtlessly be a valuable adjunct to other observations from the electron microscope. However, it is probable that a more exacting set of definitions would be required to describe the classes of fillers adequately.

Unfortunately, study of the state of aggregation of a siliceous filler by determination of the viscosity of its suspensions has been unsuccessful. Although investigation of the viscosity of silica sols has yielded much useful information, the degree of aggregation to be found in sols is much less than that found in dispersions of silica fillers, simplifying interpretation of the results with sols. Related to problems of viscosity of dispersions are those of settling of dispersions. Thus, sedimentation tests[16] have been used to determine aggregate size. In both the viscosity and sedimentation methods, the degree of aggregation of the solid in the medium depends on the amount of mechanical deflocculation the sample receives. Obviously, the extent of aggregation of the filler in an elastomer is influenced by the amount of shear experienced during mixing of filler into the elastomer. Thus, to get a comparable degree of aggregation in a liquid medium and in an elastomer appears to be difficult. No reports have indicated that viscosity or sedimentation data for fillers have been useful in the interpretation of reinforcement phenomena.

V. REINFORCEMENT

A. INTRODUCTION

In this Section reinforcement will be discussed from several viewpoints; as reflected by modulus measurements, as reflected by tensile strength, and as understood in a general sense. The contribution of silica and silicate fillers will be emphasized in illustrating principles and ideas. Examples, involving the use of other types of fillers, will be cited where required for better understanding or emphasis.

B. MODULUS REINFORCEMENT

1. *Relation of modulus to concentration and shape factor.*—One of the most obvious changes which occurs when a finely divided solid is dispersed in a rubber is a stiffening. This is analogous to a viscosity increase when a finely divided solid is added to a liquid. Smallwood[45], Guth[46,47] and Cohan[48] extended this concept to rubber.

Smallwood[45] developed an equation from an analysis of the stresses about a spherical particle. The equation related Young's modulus (stress at very small elongations) of the filled rubber, E^*, to that of an unfilled rubber, E, and the volume concentration of the filler, C. This equation

$$E^* = E(1 + 2.5C) \tag{7}$$

is analogous to the simplest form of the one developed by Einstein relating the viscosity of a liquid containing dispersed spheres.

Guth[46] used the more complete Einstein relation, the form of which was suitable for relating the viscosity, Young's modulus, and the dielectric properties of the filled rubber. The form for modulus properties is

$$E^* = E(1 + 2.5C + 14.1C^2) \tag{8}$$

Certain rubber fillers were found by Guth[47] and Cohan[48] to follow this relation for concentrations up to about 10 volume per cent. Some other fillers, not adhering to Equation (8) were found to follow more closely the analogous Einstein relation for rod-shaped particles. Equation (9), in which a

$$E^* = E(1 + 0.67FC + 1.62F^2C^2) \tag{9}$$

shape factor, F, (the length to diameter ratio of the rods) is included, gave reasonably good results for some fillers which were known to form chain-like aggregates (such as HMF carbon black). It also was found[47,48] that modulus as ordinarily determined (for example, 50 and 300% modulus were used by Cohan[48]) gave results which varied only slightly from those obtained using Young's modulus. To differentiate between the two, Equations (8) and (9) would take the form:

$$M^* = M(1 + 2.5C + 14.1C^2 + \cdots) \tag{10}$$

$$M^* = M(1 + 0.67FC + 1.62F^2C^2) \tag{11}$$

For these relations to be valid, the fillers must be completely dispersed, they must be either nearly spherical or nearly rod-shaped, there must be com-

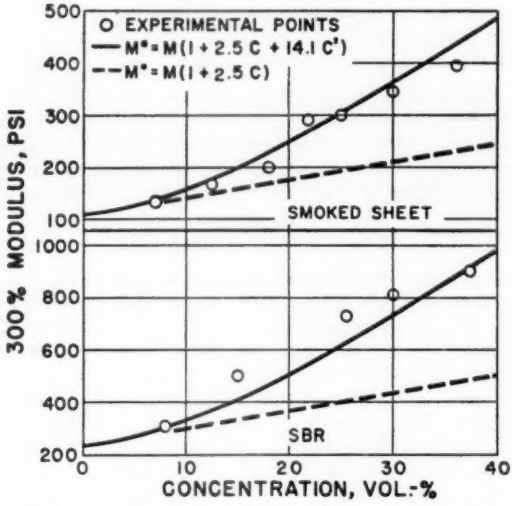


FIG. 11.—Calcium carbonate in natural rubber and SBR (data from Reference 48).

plete wetting of the filler by the rubber, and the filler concentration must be low enough that interaction between filler particles does not occur.

The Equations (10) and (11) predict the modulus for fillers which apparently meet the conditions just specified. The results of Cohan[48] are plotted for a calcium carbonate and a whiting in Figures 11 and 12. Both fillers have nearly spherical particles as observed by the electron microscope.

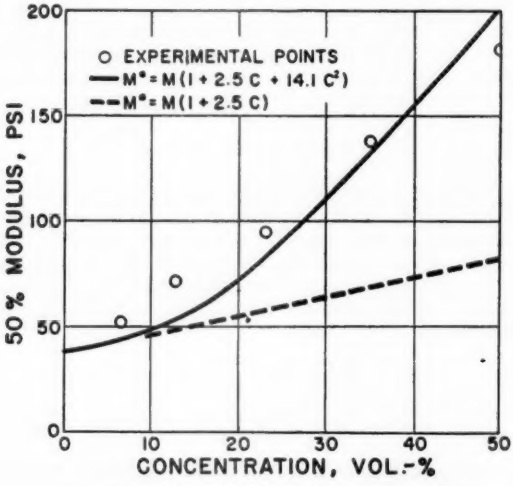


FIG. 12.—Whiting in SBR (data from Reference 48).

TABLE VII

VARIATION OF MODULUS WITH LOADING IN NATURAL RUBBER

Volume loading	Modulus, psi: Hi-Sil 101 M obs[a]	Hi-Sil 101 M calc[c]	Silene EF M obs[a]	Silene EF M calc[d]	EPC Black M obs[a]	EPC Black M calc[e]	Aerosil M obs[b]	Aerosil M calc[c]
0	500	500	200	200	300	300	530	530
10	775	695	350	300	550	580	650	740
20	875	1030	625	560	1050	1010	930	1090
30	1250	1510	950	990	1900	1880	1520	1600

[a] Data from Table V of Reference 49.
[b] Data from Figure 2 of Reference 50.
[c] Calculated from Equation (10).
[d] Calculated from Equation (11), with $F = 4.5$.
[e] Calculated from Equation (11), with $F = 5.3$.

These empirical modulus relationships can be applied to depict the behavior of other fillers as well. The data reported[49] for Hi-Sil 101, Silene EF and EPC black are reproduced in Table VII. Also included are the calculated 300% modulus using Equations (10) and (11).
and (11).

Hi-Sil 101 and Aerosil vulcanizates most closely follow the relation for spherical particles, while those containing Silene EF and EPC black follow that for rod-like particles. The calculated data for the latter two are those assuming a value of F which gives the best fit. The values of the shape factor are considered improbable. Cohan and Spielman[51], for example, have reported a value of 1.5 for fine particle calcium silicate on the basis of electron-microscope measurements. Silene EF reported by Allen, Gage and Wolf[49] is a pigment of smaller particle size than the filler used by Cohan and Spielman[51].

Also to be considered is a possible difference in shape factor exhibited by a filler in the dry state as compared to the same filler when dispersed in rubber.

TABLE VIII

PROPERTIES OF OXIDE SAMPLES

Sample	Crystal structure	Particle size, mμ	Specific surface m^2/gm: E.M.	Specific surface m^2/gm: BET	Shape factor F
SiO_2: 1	Noncrystalline	11	215	205	2.3
2	Noncrystalline	16	140	—	2.6
3	Noncrystalline	21	107	116	5.2
4	Noncrystalline	99	22	—	4.5
5	Noncrystalline	171	15	19	5.0
TiO_2: 1	Tetragonal	13	81	58	4.2
2	Tetragonal	18	61	—	4.4
3	Tetragonal	23	50	—	4.9
4	Tetragonal	72	14	—	3.0
5	Tetragonal	151	9	—	3.5
6	Tetragonal	152	9	—	5.5
7	Tetragonal	223	6	10	4.7
Al_2O_3:1	Cubic	15	91	88	3.6
2	Cubic	16	75	—	3.7
3	Cubic	17	67	—	4.3
4	Cubic	142	7	—	5.3
5	Cubic	189	5	13	4.8
Fe_2O_3:1	Rombohedral	21	51	53	4.0
2	Rombohedral	175	6	—	5.0
3	Rombohedral	326	3	4	5.2

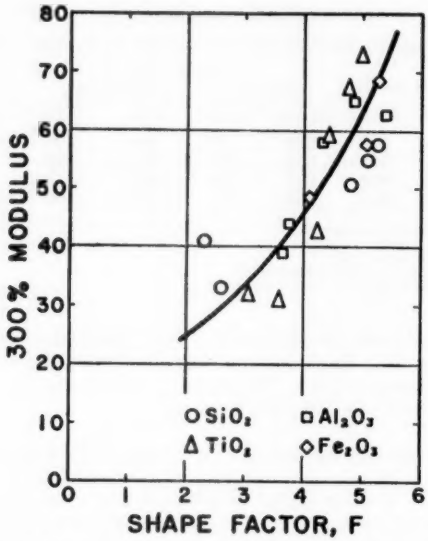


FIG. 13.—Modulus as a function of the shape factor F at 11 volume loading (data from Reference 52).

It is possible that a greater structure formation will appear in the rubber than is exhibited by the dry filler.

A rather thorough study of filler reinforcement by fine particle silicas and other fillers has been reported by Flemmert[52]. Well-defined fillers were prepared. They consisted of silica, alumina, iron oxide and titanium dioxide possessing particle diameters ranging in size from 11–326mμ. Further characterization included surface area, particle shape and the shape factor as calculated from electron microscope measurements. Data on these fillers are reproduced in Table VIII.

Flemmert[52] evaluated his fillers in formulations so that, with the testing methods employed, he encountered few variations which could be blamed on the effect of filler upon cure. He concluded that at the 11 volume loading used optimal results could be obtained in natural rubber for all the fillers considered.

In agreement with the viscosity-type relationships, modulus was found not to be dependent upon the particle size of the filler. Modulus was found to be a function of shape factor F, Figure 13. Dependence of elongation at break and

TABLE IX

CHARACTERIZATION OF FILLERS

Filler	Chem. compn.	Specific vol. (cc/g)	Surface area (m^2/g)
Santocel-CS	Silica	0.439	135
Aerosil	Silica	0.457	212
Carrara	Silica	0.364	4.04
Celite-270	Diatomaceous earth	0.456	5.54
Alon-1	Alumina	0.300	48

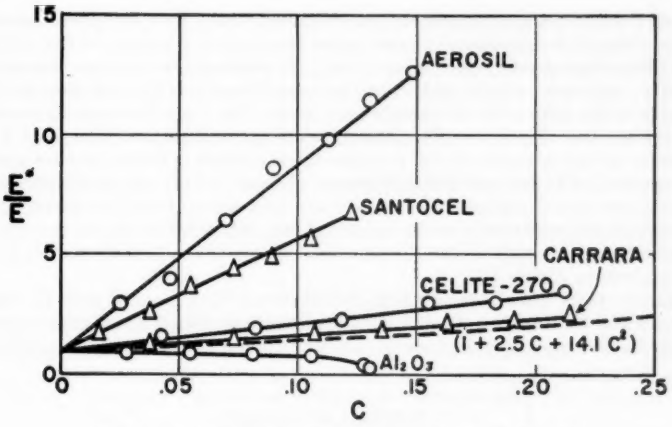


FIG. 14.—Relative modulus, E^*/E, vs. volume fraction of filler, C (data from Reference 53).

hardness on the shape factor was also observed. Additional results of this work will be treated in Section V—C, Tensile Reinforcement.

Bueche[53] observed the performance of a number of fillers in polydimethylsiloxane vulcanized with benzoyl peroxide. The physical properties of the fillers are listed in Table IX.

The data obtained by stress measurements using the fillers listed in Table IX were compared[53]. The curves shown in Figure 14 compare the data for the various fillers with Equation (8). It can be seen that large deviations from theory occurred with the fully reinforcing fillers. Further doubt of the validity of Equations (8) and (9) for predicting the modulus of filled elastomers is apparent from the data in Table X. The shape factors required for the application of Equation (9) were not considered by Bueche to be realistic.

Bueche expressed no surprise at the failure of Equations (8) and (9) to be reliable for reinforcing fillers. He argued that in the presence of filler-polymer attachments, more elastically active chains are formed and the modulus of the elastomer changes. This is not in line with the assumptions on which Equation (8) was derived. On the other hand, he points out that where no filler-polymer interactions occur, the stress analyses leading to Equation (8) are not valid.

Ignoring the small contribution caused by the physical presence of the filler (in the absence of attachments), he derived the following equation based on the kinetic theory of elasticity:

$$\tau = 2RTv_1[H_0] + (\sigma\rho_2 f/2A)(v_2/v_1)(1 + L)]\phi(\alpha) \qquad (12)$$

TABLE X

SHAPE FACTORS FOR FILLERS IN SILICONE RUBBER

Filler	Shape factor
Aerosil	116
Santocel	69
Celite-270	15
Carrara	10

where τ is the retractive tension; α is relative length; R is the gas constant; T is the absolute temperature; v_1 and v_2 are the volume fractions of the polymer and filler, respectively; $\phi(\alpha) = \alpha - 1/\alpha^2$; H_0 contains the elements of crosslink density, molecular weight of the polymer, and density of the polymer; ρ_2 is the density of the filler; σ is the surface area of the filler; A is Avogadro's number; f is the number of polymer-filler attachments per unit area of filler; and L is a measure of the extent to which polymer loops extending from the filler surface are crosslinked to the rest of the polymer. Equation (12) was developed on the assumption that the points of adherence to a filler are added at random and that a molecule will contribute to the elasticity only when it has two or more points of adherence. A plot of the tension data obtained for Aerosil and Santocel-CS is given in Figure 15.

Linear plots were obtained also for the stress data secured with the use of Carrara and Celite-270. Except with the latter two fillers, the results obtained on the swollen and dry samples were similar. Using Carrara and Celite-270, the

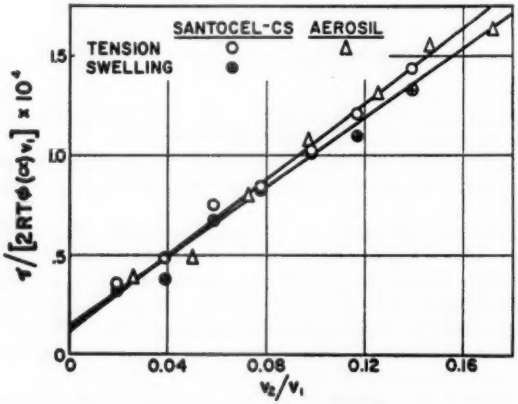


FIG. 15.—Effective crosslinks vs. volume fraction of filler for Santocel-CS and Aerosil (data from Reference 53).

lower values found with swelling are attributed to the displacement of some of the polymer from the filler surface by the solvent. The slopes of the curves were utilized to calculate values for the filler area per attachment (Table XXIX). Similar generalizations[54] were made on the behavior of several carbon blacks in neoprene.

Other investigators[55,56] also have uncovered exceptions to the early theoretical modulus—concentration relation with reinforcing fillers. As noted above, the relation is untenable in the presence of filler-polymer bonds. Zapp and Guth[55] cite the increase in stiffness and bound rubber values with time as evidence of filler-polymer interaction with active fillers. They also point out that deviations cannot be justified simply by a shape factor; that some asymmetric particles like diatomaceous earth contribute a stiffening effect but add little to the elastic or equilibrium modulus.

Rehner[57] related reinforcement and reinforcement energy by a theoretical treatment of the surface energy changes occurring on the surface of a filler.

The concept that the free energy of reinforcement is composed of the elements of surface energy and elastic energy was advanced by Weiss[58].

Zapp and Guth[55] employed an expression previously developed[59] to differentiate between filler-volume and filler-surface effects.

$$Z = Z_u + Z_s \tag{13}$$

where Z = total stress, Z_u = stress due to internal energy, and Z_s = entropy contribution.

The components of Equation (13) can be converted to the form

$$Z = Z_u + T\left(\frac{\partial Z}{\partial T}\right) L \tag{14}$$

to which experimentally determined values can be assigned. The entropy term can be evaluated from the slope of a plot of equilibrium stress and absolute temperature. These authors visualized the entropy effect as reflecting the

TABLE XI

THE INTERNAL ENERGY CONTRIBUTIONS TO TOTAL STRESS AT APPROXIMATELY 20 VOLUME LOADING OF VARIOUS FILLERS IN BUTYL

Filler	Particle diameter mμ	Total equilibrium stress, lbs/sq in	Internal energy contribution, %
HAF black	32	165	27
Calcium silicate	40–50	105	22
FF black	34	122	21
Clay	—	80	21
Calcium carbonate	87	95	19
SRF black	81	96	14
MT black	274	90	12

influence of the filler volume upon the position and movement of network segments. They associated the internal energy contribution with the restriction of polymer chains by filler forces.

At 20 volume loadings of various fillers in butyl, the total stress and internal energy contributions to the total stress, as calculated from the data of Zapp and Guth, are tabulated in Table XI.

As shown by Bueche[53], a prime requirement of any study like this is uniformity of cure effects on the filler performance. An approach to this demand was made here by the use of a butyl rubber of low unsaturation. It was reported[60] that a maximum state of vulcanization can be achieved with this elastomer where further addition of curatives does not cause an increase in network formation. Allegedly this permits the use of sufficient curatives to meet the needs of all types of fillers (but see discussion in Section V—E).

Even at the relatively low loading at which the data in Table XI were obtained, the HAF vulcanizate exhibited the greatest internal energy contribution in an absolute sense as well as percentage-wise. For the clay, calcium carbonate, SRF black and MT black compounds, the internal energy contribution listed in Table XI represents the maximum at least up to 30 volume loadings. At 30 volume loadings, however, the represented internal energy contribution of the HAF and FF black vulcanizates accounted for 45–50% of the total stress.

At the higher loading where the internal energy contribution can become important, calcium carbonate was not tested. No representative of fine particle silica was included in the study. Recent investigations at Columbia-Southern Research Laboratories confirmed the results observed by Zapp and Guth. An extension of the scope to include fine particle hydrated silica revealed that with this procedure the silica performed similar to HAF black.

The restriction to swelling by good rubber solvents of loaded vulcanizates was considered another indication by Zapp and Guth of the extent of filler action. It was found by these investigators that clay was virtually without effect. Calcium silicate and calcium carbonate filled vulcanizates, like those containing MT black, restricted swelling considerably less than the more active HAF black. As will be shown in Section V—E, adequately-cured silica vulcanizates show restricted swelling to the same extent as black stocks.

On the basis that the restriction of swelling of the respective vulcanizates, like the large contribution of internal energy, is a measure of reinforcement, calcium silicate, calcium carbonate and MT black may be considered as no more than semi-reinforcing, as compared to HAF black and fine particle silica. It becomes apparent, however, that now one section of the authors'[55] generalized

TABLE XII

CROSSLINK DENSITY OF FILLED (15 VOLUME) NATURAL RUBBER VULCANIZATES

	Crosslinks, moles/g $\times 10^4$			
	Fine particle silica[a]		HAF black[b]	
Cure, min at 287° F	Swelling	Equilibrium modulus	Swelling	Equilibrium modulus
15	0.98	0.93	0.52	0.47
30	1.22	1.46	0.93	1.02
60	1.25	1.46	0.94	1.08
120	1.14	1.35	0.85	1.02

[a] Hi-Sil 202, Altax-DOTG acceleration.
[b] Philblack O, Santocure acceleration.

conclusion: "Mineral fillers do not exhibit such persistent particle-rubber bonding. Therefore, in the field of rubber reinforcement, carbon surfaces occupy an inimitable position", does not apply to reinforcing hydrated silicas.

2. *Relation of modulus to crosslinks in filled vulcanizates which suggests filler-polymer interactions.*—Procedures which treat relationships of loaded vulcanizates on the basis of filler concentration yield information of limited significance, because they fail to connect elastic properties with network structure. On the basis of the statistical theory of elasticity, an expression was developed relating stress and strain on the basis of crosslink development[61, 63].

$$\tau = RT\nu(\alpha - 1/\alpha^2) \qquad (15)$$

where τ = force per unit initial cross-sectional area, R = gas constant, ν = number of crosslinked chains per cc, and α = degree of extension (undeformed $\alpha = 1$). ($RT\nu$ often is referred to as the "G" term relating tension and extension.)

In practice, Equation (15) applies well to unreinforced rubber only at low extensions. Mullins[64] reported that the expression also described the behavior of reinforced rubber at low extensions following large prestresses. With appropri-

ate modification, Equation (15) is more applicable to reinforced rubbers relaxed by swelling[65].

The modified expression has been useful in recent investigations relating reinforcement and vulcanization to network structures[66, 67]. Application[68] of Equation (15) to relaxed filled vulcanizates offered additional support to cross-link values obtained by swelling[69]. Comparative data are shown in Table XII.

An expression has been presented[70] which permits the adjustment of stress-strain curves of filled vulcanizates to fit theoretical curves.

$$\tau = 2(\alpha - 1/\alpha^2)(C_1 + C_2/\alpha) \tag{16}$$

where τ and α have the usual connotation (see Equation 15) and C_1 and C_2 are constants; C_1 is a function of the degree of vulcanization and C_2 is a constant which describes departures from simple kinetic theory*. The values for C_1 and C_2 for some filled vulcanizates are tabulated in Table XIII[71].

The authors[71] feel that the values of C_1 and C_2 pertain to the "soft" regions of the filled stocks. "Soft" areas not already present form as a result of deformation. For accelerated sulfur-cured gum compounds C_2 retains the value of 1.0 kg/cm^2. Differences in C_1 shown in Table XIII are attributed to the

TABLE XIII

VALUES OF C_1 AND C_2 FOR NATURAL RUBBER VULCANIZATES

Filler	Loading, phr	C_1 kg/cm	C_2 kg/cm
MPC black	50	1.0	1.0
EPC black	50	0.9	1.0
HAF black	40	1.3	1.0
Magnesium carbonate	40	1.0	1.0
Calcium silicate	40	0.65	1.0
None	—	1.2	1.0

degree of vulcanization of the gum compound and related to differences in compounding ingredients. There is no consideration of bonds between filler and rubber in this treatment.

Blanchard and Parkinson[56] also have attempted to develop empirical relationships to describe a greater portion of the stress-strain curve of reinforced vulcanizates after deformation. Based on kinetic theory, they introduced two curve-fitting parameters for an expression in which the "G" term (see Equation (15)) was defined as comprised of contributions from the number of strong linkages, G^*, and from the strength and number of weak linkages:

$$G = G^* + G_r F(X) \tag{17}$$

where G_r is proportional to the number of weak linkages and $F(X)$ represents the distribution of linkage strengths as determined by the magnitude of the prestress. A corrective factor[72] $(1 + V)$ was added to account for filler concentration. Also, from the value of $(1 + V)$ G^* was subtracted the G^* value for the gum stock in an attempt to appreciate the contribution of filler to strong linkages. In Table XIV are results reported by Blanchard for a number of

* Note added in proof. Very recent evidence indicates that C_2 is a measure of the deviation from equilibrium conditions of stress-strain and *not* deviation from the kinetic theory of rubber elasticity; Ciferri, A., and Flory, P. J., *J. Appl. Phys.* **30**, 1498 (1959).

TABLE XIV

STRONG LINKAGES DUE TO FILLER AT 26 VOLUME LOADING IN NATURAL RUBBER

Filler	Mean particle diameter, mμ	Strong linkages $(1+V)G^*-3.7$
HPC black	24	1.6
Graphon	25	0.5
HAF black	27	2.4
FF black	32	1.4
SRF black	80	1.8
Calcium silicate	30	0.2

fillers. Acceleration (Santocure) was varied according to the demands of the fillers.

To Blanchard and Parkinson the information in Table XIV indicated a criterion for reinforcing fillers; viz., that strong filler-polymer linkages are formed. The low number of such linkages for Graphon and calcium silicate were quite conspicuous and in line with the limited reinforcement generally attributed to these fillers. However, there appears to be only limited discrimination possible from the magnitude of the strong linkages. While the most highly reinforcing filler (HAF black) exhibits the greatest extent of strong bonding, the remaining fillers in Table XIV cannot be arranged properly in the usual order of reinforcement using only the ability for strong bonding.

TABLE XV

STRONG LINKAGES DUE TO SILICA AT 15 VOLUME LOADING IN NATURAL RUBBER

Filler	$(1+V)G^*-2.7$
Hi-Sil 202[a]	2.9
HAF black[b]	2.5

[a] Altax-DOTG acceleration.
[b] Santocure acceleration.

There is evidence that fine particle silica fillers also have the ability to form strong filler-polymer bonds, Table XV[73].

In his further concern over the number and strength distributions of secondary linkages, Blanchard[74] finds no correlation with particle diameter of the filler. His energy data suggests that these weaker linkages, broken by prestress, are formed by physical attachments involving a number of chemical groups in the long chain polymer molecules. A tabulation of the values of $(1 + V)H/\Omega\ (X)$, proportional to energies of breakage, and the number of weak linkages, $(1 + V)\ G_r$, is given in Table XVI.

Furukawa and others[75] attempted the determination of the filler contribu-

TABLE XVI

STRENGTH AND NUMBER OF WEAK LINKAGES IN FILLED (26 VOLUME) NATURAL RUBBER VULCANIZATES (SANTOCURE)

Filler	Particle diameter, mμ	$(1+V)H/\Omega(X)$	$(1+V)G_r$
HAF black	27	0.083	4.8
MPC black	25	0.081	4.5
Graphon	25	0.050	2.6
Calcium silicate	30	0.062	3.8

tion to strong bonding for a number of fillers in natural rubber. They ascertained that below the volume fraction of filler of 0.20, the concentration of crosslinks, as calculated from swelling or equilibrium modulus, is a linear function of loading. Then by a consideration of the difference between the crosslinks as measured by equilibrium modulus and swelling, the extrapolation of these values to zero loading, and comparison with the crosslink density of the respective unfilled compounds, some measure of the effect of the fillers on cure and their contribution to the crosslink level could be surmised. Of added interest is the extent of increased crosslink levels of the filled stocks over those of the gum vulcanizate, Table XVII.

The data in Table XVII is evidence that the crosslink density of fine particle silicate and silica-filled vulcanizates can be comparable to that realized in black stocks.

As in the work of Blanchard and Parkinson[56], strong linkages found here did not generally reflect reinforcing ability. Furukawa attributed this primarily to the effect of the filler on vulcanization. Such filler effects cannot be ignored as a factor in reinforcement (see Section V—E). Equally hazardous is the selection of a single cure to represent the behavior of the filled vulcanizate. It should not be inferred, therefore, that the crosslink values of Table XVII are

TABLE XVII

CROSSLINK VALUES IN THE PRESENCE OF FILLERS AT 0.10 VOLUME RATIO OF FILLER

	Crosslink density, moles/g $\times 10^4$		
	Filled compound, cure, 15 min. at 131° C		
Filler	By equilibrium modulus	By swelling	Unfilled compound*
HAF black (Tokai)	10.9	8.6	9.3
Aluminum silicate (Frantex)	10.8	8.1	8.8
Silica (Nisil)	14.6	11.3	9.0

* Value the same by modulus or swelling.

representative of those obtainable for a given filler. The factors already discussed, as well as the individual curing system, must be considered in the comparison of the reinforcing ability of fillers.

Reflecting concern over the contribution of filler-polymer linkages to modulus, Stearns and Johnson[76] attempted an interpretation of modulus reinforcement in a manner quite similar to that of Blanchard and Parkinson[56]. After preliminary stressing to eliminate the softening effects, an equilibrium stress-strain curve can be traced. The area under this curve was found by Stearns and Johnson to be related to the filler concentration by

$$W_R = W_R^0 + \phi\left[\frac{V_2}{(1 - V_2)^2}\right] \tag{18}$$

W_R is the work of retraction (area under equilibrium stress-strain curve) for the filled rubber vulcanizate, V_2 is the volume concentration of filler, and W_R^0 is the work of retraction for the unfilled vulcanizate. The constant ϕ was interpreted by these investigators to be indicative of the specific reactivity of the filler or its capacity to form filler-polymer bonds. At least with carbon blacks, those fillers with indicated reinforcing ability showed specific reactivity towards

short-time bromine adsorption (but also see Reference 77). It seemed reasonable then to Stearns and Johnson, that the filler unsaturation participated in vulcanization with sulfur to form filler-polymer crosslinks. Observed ϕ constants for several fillers in SBR are reproduced in Table XVIII.

An explanation for the poor performance of the silica vulcanizate probably lies in the incompatibility of the curing system with the filler. This is discussed in detail in Section V—E, 3-a in particular relation to the conclusions to be drawn from the work of Stearns and Johnson.

Corroboration of the original premise that activity of the filler surface was responsible for the influence of filler-polymer linkages, as reflected by ϕ values, was implied by the effects of coating silica. Stearns and Johnson[78] found that treating silica with various organosilanes had significant consequences on the ϕ

TABLE XVIII
OBSERVED VALUES FOR CONSTANT ϕ

Filler	BET surface area m^2/g	Particle size, $m\mu$	$[\phi]_0^{125}$ (cal per cc)
EPC-2	108	29	0.37
EPC-2, calcined	112	—	0.49
Graphon	76	30	0.00
Fine particle silica	150	22	0.00

constant. Such effects depended on the structure of the organic radical (not necessarily unsaturated). This work will be treated in Section VI referring to coated silicas.

C. TENSILE REINFORCEMENT

1. *Dependence of tensile on particle size.*—One common factor which influences tensile reinforcement exists for all types of fillers, namely, particle size. For a given type of filler, tensile reinforcement varies inversely with particle size. This has been shown to apply for carbon blacks[79–82], silicas[52, 82–84], calcium carbonates[48, 51, 85], aluminum silicates[84], aluminas[52, 86], calcium silicates[51, 82], Prussian blue[52], and stannic oxide[83]. Within a group the general dependence of tensile reinforcement on particle size is apparent. Between groups the same trend has been observed, but other factors, as extent of dispersion and filler-polymer interaction, cause apparent discrepancies.

In a comparison of fillers commercially available at the time of the study (ca 1952), Flemmert[52] found some relation between particle size and tensile strength for all fillers regardless of type, when the state of aggregation was taken into account, Table XIX. He observed that when particle shape and degree of aggregation could be considered the same for different groups of fillers, the dependence on particle size was unalterable.

Flemmert then prepared samples of four types of fine particle fillers, silicon dioxide, alumina, ferric oxide and titanium dioxide, in such a fashion that the apparent state of aggregation was very low and the particle diameters could be varied over a fairly wide range (see Table VIII). With filler loadings of 11 and 22 volumes per 100 parts of rubber, it was observed that all samples having an arithmetic mean diameter smaller than 30 $m\mu$ gave vulcanizates with a tensile strength of about 300 kg/cm^2—in the range produced by reinforcing grades of carbon black. Figure 16 illustrates the change in tensile strength and tear resistance with particle size found for fine particle silica. Similar curves can be drawn for titanium dioxide, alumina and ferric oxide. There was no tendency

TABLE XIX

PARTICLE SIZE AND DEGREE OF AGGREGATION OF FILLERS. EFFECT ON TENSILE AND TEAR OF NATURAL RUBBER VULCANIZATES

		11.5 Volume			23 Volume		46 Volume	
Aggregation*	Filler	Particle diam. mμ	Tens. psi	Crescent tear lb/in	Tens. psi	Crescent tear lb/in	Tens. psi	Crescent tear lb/in
II Low	Whiting	550	3350	62	2870	67	1950	90
II Low	Barytes	500	3430	118	2840	106	2000	—
II Low	$MgCO_3$	410	3830	90	3130	112	2360	168
II Low	Lithopone	230	3920	123	3550	157	2800	258
II Low	Dixie Clay	200	3840	78	3410	112	2640	151
II Low	ZnO (ordinary)	130	3920	179	3630	342	2700	330
II Low	ZnO (fine part.)	90	3900	325	4010	420	3160	448
II Medium	Frantex B	65	4340	39	4410	62	3770	78
II High	Silene EF	43	4020	319	3630	398	—	—
II High	Hi-Sil 101	25	4170	409	3800	470	—	—
III Low	Thermax	274	3680	241	3500	308	2490	280
III Low	FT black	74	4150	353	4140	398	3040	420
III Low	EPC black	31	4170	398	4290	560	—	—
III Low	MPC black	28	4410	381	4890	655	3800	812
III Low	Aerosil	14	4550	—	—	—	—	—
III Medium	HMF black	51	3950	—	—	—	—	—
III Medium	HAF black	34	4290	—	—	—	—	—

* See Section IV—E, for definitions.

discerned for the tensile strength to reach a maximum, despite the wide range of particle sizes considered.

The tensile behavior of silica depicted in Figure 16 closely resembles that reported for carbon black [79, 80], for calcium carbonate[51] and for whiting[51]. This relationship between tensile strength and particle size apparently holds only for optimum loadings, however. Evidence exists[83, 50] that the loading for maximum tensile strength decreases with decreasing particle size. This reportedly becomes most pronounced at particle sizes below 50 mμ.

A dependence of the loading for maximum tensile strength on the particle size of the filler would indicate that the number of filler particles is important.

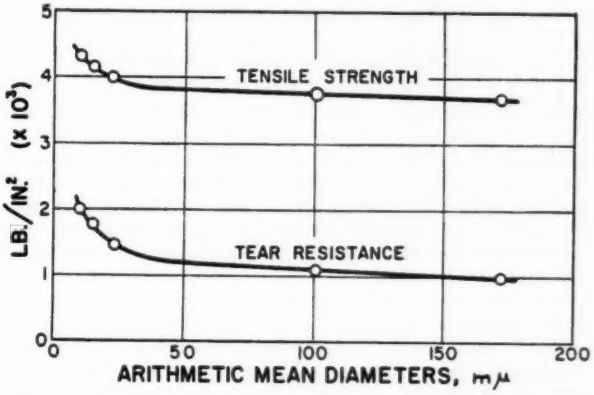


FIG. 16.—Tensile strength and tear resistance as functions of the particle size of the filler at 22 volume loading (data from Reference 52).

The particle diameter determines the number of particles per unit volume at a specified loading. This would be consistent with the mechanical picture set forth by Flemmert to explain increased tensile strength, Figure 17.

Flemmert envisions the possibility of filler particles which are too large for rubber chains to envelop. However, when the size of the particle approaches a certain ill-defined critical size, the particles can then fit within crosslinked segments in the vulcanized rubber. In Figure 17A three chains of rubber crosslinked together are shown. When natural rubber is stretched crystallites develop, which tend to reinforce the rubber. This is depicted in Figure 17B. Filler particles which are sufficiently small can be accomodated within the crosslinked segments as represented by Figure 17C. Upon applying a stress, the filler particles effectively take up the slack in the crosslinked chains permitting a greater degree of crystallization, Figure 17D. The schematic representation is similar for noncrystallizing rubbers, such as SBR, except that in the stretched, unfilled rubber there is no reinforcement through crystallization. Fillers can

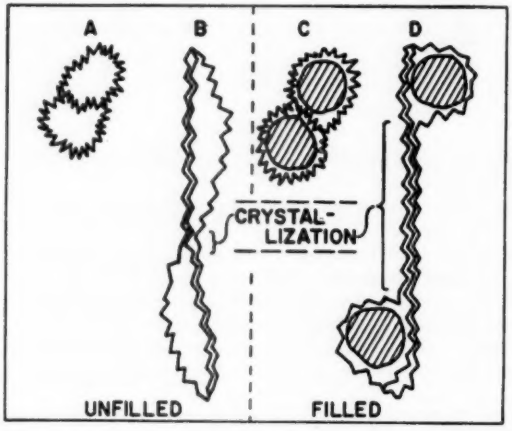


FIG. 17.—A schematic diagram of the stretching process in natural rubber with active fillers according to G. Flemmert, Reference 52.

still contribute to reinforcement in these rubbers by promoting more favorable conditions for crystallization, as represented by Figure 17D. By this simple picture, the capacity of a filler to distribute the stress between two adjacent chains is independent of the formation of any filler-polymer linkages.

Flemmert also suggested that aggregation of the filler into larger particles would lower its reinforcing value. In his opinion, a chain-like aggregation, however, would be beneficial by effectively crosslinking several polymer units like those shown in Figure 17D.

Recent data by Dogadkin and his co-workers[41, 42] seem to support Flemmert. The former investigators prepared silicas which they identified as "active", "medium active" and "inactive" on the basis of their behavior towards water adsorption and on the physical properties, tensile strength, tear resistance, and modulus, of the respective vulcanizates. It was reported that below 40 volume loadings of the "active" silica, extraction of the filler by dilute sodium hydroxide

TABLE XX

"ACTIVE" AND "INACTIVE" SILICA FILLERS IN POLYBUTADIENE

Filler*				Sodium hydroxide extraction of silica at 25 vol. loading, %	Vulcanizate*		
Type	SiO_2 %	Surface area, m^2/g	Water adsorption, ml/g		Tensile kg/cm²	300% Modulus kg/cm²	Tear kg/cm²
"Active"	82	61	1.5	50	116	59	43
"Inactive"	84	50	0.90	0	41	44	25

* Details of silica preparation, the particle size of the filler, vulcanization system, or filler loading in vulcanizate not disclosed in Reference 41 or 42.

from the two component filler-polybutadiene mixture was relatively rapid. Conversely, the rate of extraction of the "inactive" filler was almost nil. Results of the study with the "active" and "inactive" silicas are tabulated in Table XX. For a more detailed discussion of filler aggregation see Section IV—E.

The information in Table XX was interpreted[41, 42] as showing that the "active" fillers were present as chain structures[87]. Such structures would be expected, by Flemmert's model, to aid in tensile development and to make the silica more accessible for extraction by alkali. It should be noted that the particle size of the fillers was not described. In view of the low surface area reported, the fillers would be expected to have a particle size in excess of that usually found in a fully reinforcing grade silica[88].

An example of the damaging effects of aggregated filler was described for silica in silicone rubber[89]. Aggregate structure can be introduced into a fine silica filler by ball milling before incorporating it into the polymer. Apparently welding of particles occurs to yield porous aggregates. Table XXI lists data from silicone vulcanizates respectively containing pyrogenic silica before and after ball milling[89]. While the surface area of the porous materials was not altered seriously by ball milling, aggregation was increased and tensile strength suffered.

Treatment of fine particle hydrated silicas with unsaturated organosilanes was found to increase tensile strength but reduced tear resistance[90] of the SBR vulcanizates. This was attributed to the destruction of structure in the filler by coating.

2. *Requirement of filler-polymer interaction for maximum tensile in filled vulcanizates.*—Working with silicone rubber, Warrick and Lauterbur[89] obtained data on vulcanizates which contained several different fillers. The fillers included titanium dioxide, alumina, calcium carbonate and a variety of silicas, all at 15–25 volume loading. Only a general dependence of tensile on particle size was noted.

In the search for the source of other influences of filler on tensile strength besides particle size, it was observed that modification of surface chemistry produced profound effects. For example, treatment of silica with ammonia

TABLE XXI

EFFECT OF BALL MILLING SILICAS TO PRODUCE AGGREGATION

	Surface area, m^2/g	Particle size, mμ	Tensile psi
Before ball milling	125	21	4560
After ball milling	101	150	856

TABLE XXII

INFLUENCE OF OH CONCENTRATION ON SURFACE OF FILLERS ON THE TENSILE OF SILICONE VULCANIZATES

Silica	Average part. size mμ	Surface area, m^2/g	Relative surface OH*, $g/m^2 \times 10^5$	Tensile at ultimate cross section, psi
Dupont GS199S	12	274	1.90	8890
Aerosil	21	133	5.64	4560
Santocel C	24	121	7.11	2390
Linde	17	161	8.39	3060
Vycor glass powder	88	34	13.20	1585
Hydrolyzed $SiCl_4$	45	75	43.80	270
Unfilled	—	—	—	75

* By means of Karl Fischer reagent.

resulted in a 75% reduction in the tensile strength of the cured silicone[89]. Warrick and Lauterbur[89] also found better agreement of tensile strength with relative hydroxyl concentration of the filler than with particle size, Table XXII.

Interestingly, Dupont silica GS199S whose vulcanizate exhibited the highest tensile strength contained an alkoxy coating. Upon heating the filled compound for 24 hours at 250° C, the coating was destroyed and the tensile strength became one of the lowest. As will be shown in Section VI, modification of silica surfaces by coating often leads to higher tensiles in a variety of polymers.

The preceding information on the effects of filler surface chemistry, suggests that tensiles are influenced by some type of filler-matrix restriction of a chemical nature. Bueche[91] investigated the structural requirements for highest tensiles in SBR gum and filled vulcanizates. Like Flemmert[52], he considered that, to a first approximation at least, the effects of fillers and crystallization are to increase the number of chains which share the load of a broken chain, Figure 18. Equation (19) was derived to describe this process.

$$\text{Tensile strength} = (\nu_e/3)^{\frac{1}{3}} F_c[1/(1 + 0.61X) - q] \qquad (19)$$

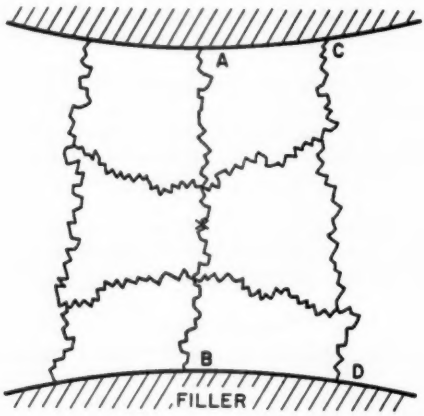


FIG. 18.—A schematic diagram to show the action of reinforcing fillers according to F. Bueche, Reference 91.

where $X = 2(aF_c/KT\epsilon)^{\frac{1}{2}}$, ν_e is the effective number of network chains in unit volume, F_c is the force which will break the weakest chain length, ϵ is the average number of possible crosslink sites between actual crosslinks, and "a" is the length of a chain segment. The quantity q, which of course would be 0.5 for gum stocks, is equal to the fraction of the extra load shared by each neighbor of the chain broken. In the presence of 50 phr HAF black, $q = 0.28$; in the presence of 55 parts of calcium carbonate, q approximates 0.5.

Figure 18 illustrates one of the many possible ways in which fillers and crystallization can act. When chain AB breaks at X, less than half the load held by this chain will be transferred to chain CD. Part of the load is held by the crystal or particle which distributes it over a number of chains. This requires that q in Equation (19) is less than 0.5. If the filler does not interact with the rubber, q would be 0.5.

TABLE XXIII

TENSILES OF RADIATION- AND SULFUR-CURED SILICA[a] FILLED (30 VOLUME) NATURAL RUBBER VULCANIZATES

Maximum tensile, psi	
Radiation cure[b]	Sulfur cure[c]
2830	4130

[a] Hi-Sil 233.
[b] Cured in 1 Mev resonance transformer.
[c] Thiazole-guanidine cure.

3. *Effect of bond type on tensile.*—Implicit in the discussion of filler effects on tensile which suggest filler-polymer interactions of some type, is the concept that the nature of the linkages, filler-polymer, or polymer-polymer, cannot be ignored. This immediately involves a consideration of the relative influences of the curing system which creates the crosslinks. Such influences, as reflected by network development in silica filled vulcanizates, will be discussed in some detail in Section V—E. As influencing tensile, some recent opinions will be recorded here.

TABLE XXIV

STRESS RELAXATION OF METAL OXIDE VULCANIZED BUTADIENE-UNSATURATED ACID COPOLYMER

Metal Oxide	Time for stress to decay to half the initial value at 21° C
Magnesium oxide	4 hours
Zinc oxide	16.5 minutes
Lead oxide	10 minutes

During the course of their investigation of the crosslinking of silica and carbon black filled natural rubber vulcanizates by radiation, various investigators have observed reduced tensiles as compared with usual sulfur vulcanizates[92–94]. A similar behavior was observed by Gee[95] for peroxide cures. The extent of the difference in the influence of radiation and sulfur cures on the tensiles of silica-filled vulcanizates can be seen from the data in Table XXIII[92].

Pinner[94] discusses this phenomenon. According to him, the failure of peroxide and radiation-cured vulcanizates to crystallize can hardly be attributed in this case to high modulus. Comparison with the behavior of normal sulfur cures forces the conclusion that the presence of easily broken and reformed poly-

sulfide bonds is responsible for the higher tensile strength of the sulfur cured compounds. Experience with carboxylic polymers suggests that the capacity for a crosslink to yield under stress, to allow chain alignment for crystallization, and then be able to reform, results in the highest tensile strength, Table XXIV[96].

Carboxylic elastomers can be cured with sulfur or by means of metal oxides. The sulfur crosslinked vulcanizates exhibit tensiles similar to those found with the sulfur-cured noncarboxylic analogs. On the other hand, the metal oxide cured compounds are characterized by extremely high tensiles (in the range of 8000 psi)[97, 98].

The information in Table XXIV, considered with evidence that the tensile strengths of the zinc oxide or lead oxide cured vulcanizates are considerably higher than the tensiles of the magnesium oxide cured carboxylic rubbers[97], illustrates the importance of the nature of crosslinks on tensile development. The significance of crosslink structure as well as the implied ability to undergo exchange reactions at the crosslink site is reflected in the behavior of other polymer systems also. For example, the reaction product of polyesters and diisocyanates relaxes under stress thirty times faster than the relatively weak peroxide crosslinked analog[99].

D. FILLER–POLYMER INTERACTION DURING REINFORCEMENT

1. *Evidence of filler-polymer bond formation during vulcanization.*

a. Evidence for filler-polymer bond formation in filler-tensile and filler-modulus relationships of vulcanizate.—Evidence has been presented that the physical presence of a fine particle filler is necessary to secure high tensiles in vulcanizates by crystallization, but that the modulus-filler concentration relationship based on viscosity relations fails in the presence of an active filler. A well-formed network is necessary to eliminate plastic flow and produce good tensile strength, but an overly high crosslink density reduces tensile strength by impeding polymer chain alignment and subsequent crystallization. A filler-polymer bond of adequate strength is thought necessary for high tensiles, but there is evidence that such a bond under high tension should have the property of controlled "slip" on the surface of the filler and be able to reform. The failure of reinforcing fillers to conform to the modulus-concentration relationship found for inert materials and the large contribution of internal energy to the total stress of reinforced vulcanizates—these results, along with the tensile concepts, suggest the presence of filler-matrix restraints in vulcanizates containing reinforcing fillers.

Filler-polymer bonds are difficult to differentiate and to identify with available techniques. As will be discussed later, the increase in the number of total crosslinks in a vulcanizate accompanying the use of a filler is thought to be due to added filler-polymer crosslinks or due to the effects of a catalytic influence of the filler on the rate of total crosslink development. There has been considerable effort made to separate the two effects; to verify the existence of filler-polymer bonds; and to define their nature.

b. Evidence for filler-polymer bond formation in effects of chemical modification of filler surfaces on vulcanizate properties.—As mentioned in a previous section, Stearns and Johnson[76] offered proof for the presence of filler-polymer bonding in black loaded vulcanizates. Further evidence for filler-polymer interactions in the cured compounds can be found in the effect on their properties of surface modification of the filler, of prior treatment of filler-polymer

mixtures, and of the use of elastomers containing different functional groups. Assurances must be made that such effects are not just the result of the influence of physical changes in the filler or the result of influences on the curing system.

Beebe and his co-workers[100] investigated the effects of heating and partially graphitizing an MPC black on the properties of the respective vulcanizates. Their results, tabulated in Table XXV, testify to the consequences of changing the chemical nature of the filler while keeping the physical characteristics apparently constant.

TABLE XXV

EFFECTS OF HEATING AND PARTIALLY GRAPHITIZING AN MPC BLACK (45 PHR) ON THE PROPERTIES OF NATURAL RUBBER VULCANIZATES

	Physical properties		Vulcanizate properties at optimum cure	
Treatment	Particle[a] diameter A	Surface[b] area, m^2/g	Tensile, psi	300% Modulus, psi
None	285	110	4300	1720
Devolatilized at 927° C	285	120	4300	1940
Heated at 3200° C	300	85	3800	230

[a] Measured by electron microscope.
[b] Measured by BET method.

The data in Table XXV show that merely devolatilizing the surface had no effect on the properties listed. More vigorous heating effected a dramatic reduction in modulus but did not change the tensile strength appreciably. Apparently the partially graphitized filler still produced filler-polymer attachments of sufficient strength (but less in number)[67] to permit maximum tensile development.

Brooks[90] and coworkers observed the effects on filled SBR 1500 vulcanizate properties of treating fine particle silica with unsaturated silanes, Table XXVI.

Here again tensile remaind relatively unaffected, as expected, and evidence of an enhanced degree of filler-polymer interaction is reflected by the increased modulus.

TABLE XXVI

FINE PARTICLE SILICA TREATED WITH ALKENYLSILANE IN SBR 1500 VULCANIZATES

	Properties of vulcanizate, psi	
Coating	Tensile	300% Modulus
None	2660	700
Vinylsilane	2990	1250

Other investigators also have reported various effects of changes in the surface chemistry of fillers, black or white, on vulcanizate properties[78, 101–105].

The treatment of filler-polymer masterbatches with various "promoters", or by heat, was claimed to cause enhanced properties of the cured stocks[106–108]. Tabulated in Table XXVII are the consequences on the properties of a butyl vulcanizate of milling a fine particle silica (Hi-Sil 202) at 310° F with 1% quinone dioxime dibenzoate[108].

It is conceivable that some of the improvements suggested by the data in Table XXVII can be explained on the basis of improved dispersion of the filler by the heat treatment. A consideration, however, of the large effect realized,

TABLE XXVII

EFFECT ON PROPERTIES OF BUTYL VULCANIZATE OF HEAT TREATMENT OF FINE PARTICLE SILICA (50 PHR) IN PRESENCE OF QUINONE DIOXIME DIBENZOATE

Filler	Bound rubber, % on polymer	Properties of vulcanizate, psi	
		Tensile	300% Modulus
Untreated	ca 10	2445	255
Treated	40	3110	1025

the participation of the oxime ester, and the increased amount of bound rubber, encourages speculation that chemical filler-polymer interactions are involved and realized in the vulcanizate.

c. Evidence for filler-polymer bond formation found in specific behavior of various fillers in specific elastomers.—Convincing evidence of the presence of filler-polymer bonds also is found in the contrasting effects of a filler in various elastomers. Some of these effects on the physical properties of the cured, filled compounds are tabulated in Table XXVIII[109].

Polymers would be expected to exhibit different effects on cure, depending on the nature of the functional groups present. When these effects are minimized by adjustments in vulcanization ingredients, however, large differences in the behavior of the filler persist[110]. Such results connected with relationships between specific fillers and polymers possessing specific chemical groups can be interpreted best by assuming the presence of filler-polymer interactions in the vulcanizate.

In their earlier investigations, Dogadkin and others[93] showed that both filled and unfilled sulfur vulcanizates, prepared under the same vulcanization conditions, have the same rate of chemical relaxation. Vulcanizates crosslinked by radiation, however, were found to perform less uniformly. The irradiated filled vulcanizates relaxed at a much lower rate than the unfilled mixtures, and differences appeared between channel and furnace blacks. These results were reported as indicating the formation of chemical bonds between filler and polymer during irradiation vulcanization.

Indications for attachments between filler and polymer have been observed for silica-filled silicone rubbers. Filled polydimethylsiloxane increases in viscosity more rapidly upon standing than does the unfilled elastomer[53]. Little, if any, polymer can be leached out of the filler-polymer mixture by the use of a

TABLE XXVIII

FINE PARTICLE SILICA AND CARBON BLACK IN VARIOUS ELASTOMERS

Elastomer	Filler	Physical properties		
		Tensile, psi	Modulus, psi	Hardness, Shore
Natural rubber	Silica	3400	730	77
(30 Vol.)	EPC black	4200	1720	71
SBR	Silica	3750	1060	80
(30 Vol.)	EPC black	4110	1930	75
Butadiene-acrylo-	Silica	4130	1370	85
nitrile (30 Vol.)	EPC black	2320	1450	68
Neoprene WRT	Silica	4440	1600	61
(30 Vol.)	MPC black	3670	1520	61

good solvent for the polymer[89], and there is a limit to the amount of filler that can be incorporated into the polymer by the usual methods. The silica-silicone relationship occupies a special position in filler-polymer affairs became a less ambiguous path is available for some of the filler-polymer interactions. Like unsaturated polymers, silica-filled silicones may contain bonds such as those formed by adsorptive forces between polymer and filler and those created by the curing system between the filler and the organic ligands in the polymer. In addition, however, siloxane rearrangements[111] between filler and polymer permit linkages of a more obvious nature[89], as indicated in Figure 19.

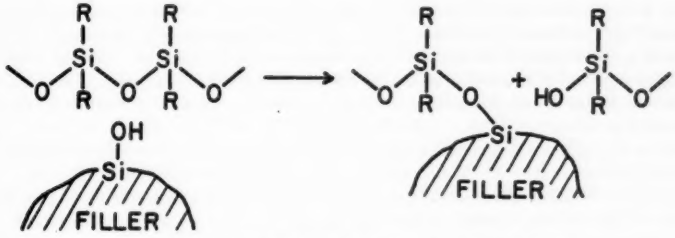


FIG. 19.—Illustration of linkages for a silica-filled silicone rubber.

The decrease in swelling of silicone rubbers containing silica fillers also suggests the presence of filler-polymer attachments, especially since it was shown[112] that the peroxide curing agent formed crosslinks at a rate independent of the filler concentration. Bueche[53] then confirmed his hypothesis, Equation (12), based on the kinetic theory of elasticity that the stiffening and swelling behavior could be explained on the basis of filler-polymer attachments. The area for such attachment was calculated for a few fillers, Table XXIX.

The relatively nonporous fillers, Carrara and Celite-270, are more efficient in forming filler-polymer attachments than are Santocel-CS and Aerosil. This behavior is attributed to the effect of small pores in the latter fillers.

TABLE XXIX

AREA OF ATTACHMENT OF FILLER–POLYMER LINKS IN FILLED SILICONE RUBBER VULCANIZATES

Filler	Surface area, m^2/g	Area on filler per attachment, $1/f$, A^2
Santocel-CS	135	28
Aerosil	212	41
Carrara	4.04	4.8
Celite-270	4.54	2.2

d. Nature of filler-polymer bond not elucidated by nuclear magnetic resonance measurements.—Any consideration of the nature of the filler-polymer linkages in unsaturated polymers increases the complexity of the problem enormously. Although evidence is emerging on the chemical nature of polymer-polymer crosslinks in unfilled compounds[113–115], the conclusions of recent workers[116, 117] investigating filled and unfilled vulcanizates by means of nuclear magnetic resonance techniques have not clarified the situation. The examination of unfilled natural rubber sulfur-cured vulcanizates (apparently contain-

ing no zinc oxide or accelerator) by Gutowsky and Meyer[116] suggested that crosslinking is not the primary mechanism of vulcanization. Honnald and coworkers[117] confirmed the findings employing normal accelerated vulcanizates. These investigators could detect no effect of carbon black loadings in addition to that observed for unfilled compounds. In a plot of line-width against temperature, the values for an unfilled butyl gum compound and for the vulcanizates containing, respectively, three carbon blacks fell neatly on the same line.

2. *Evidence for the ability to form filler-polymer attachments found in the phenomenon of bound rubber formation.*

a. Correlation reported between extent of bound rubber formation and vulcanizate properties.—Evidence on hand, then, suggests the presence of some kind of a filler-matrix restriction in a reinforced vulcanizate. Along with the necessary physical characteristics involving particle size, aggregation, etc., the ability to form an ill-defined bond with the rubber seems a requirement of a practical reinforcing filler. The chemistry of the filler which allows such a reaction also effects the crosslinking mechanism, which in turn, helps create the filler-polymer bond. As would be expected, fillers of vastly different chemical composition exhibit great differences in their effects on a given curing system. These effects, in an incompatible curing system, would obscure the potential of a physically acceptable filler to participate adequately in the important filler-polymer interactions. It is possible to classify a filler outside of the vulcanizate, on the basis of physical attributes required of a reinforcing filler such as particle size (electron microscope) and surface area (nitrogen adsorption). It would be desirable to have a procedure in which the ability of a filler to undergo filler-polymer interactions could be evaluated independent of curing system influences. The phenomenon of bound rubber development by fillers, which occurs on milling or heating filler in unsaturated elastomers (preferably in an inert atmosphere), is potentially valuable as such a procedure[118].

The extent of the development of filler-polymer gel on milling or heating various carbon blacks in elastomers has been correlated with an increase in modulus[107, 119, 120], a decrease in laboratory abrasion[120, 122] of the vulcanizate and increase in the tire wear expectancy[123–127]. Endter[128] states that the capacity of a filler to form bound rubber may be taken as an indication of its ability to reinforce. Little has been reported on bound rubber formation with fine particle silica and silicate fillers and its relation to vulcanizate properties.

b. Relationships of filler and polymer in bound rubber development.—Depew[129] observed that unvulcanized rubber pigmented with zinc oxide (150 mμ) was insoluble in benzene. Later it was reported by Menadue[130] that it was possible to form insoluble rubber by milling large volumes (up to five hundred parts filler per one hundred parts rubber) of such fillers as magnesium carbonate, magnesium oxide, zinc oxide, zinc carbonate, and lead oxide into natural rubber. Of particular hazard in assigning any mechanism to bound rubber formation is the observation recorded by Menadue of the retention of gel structure after removal of fillers with acetic acid. The information reported, however, reveals the formation of the small amount of insoluble rubber expected for normal loadings of such large particle size fillers. Also, there was sufficient ash (1–3%) remaining in the acid extracted gel to account for necessary filler attachments.

Dogadkin and his coworkers[41] recently observed an effect with several types of silica fillers similar to that reported by Menadue with his "powders". The Russian investigators, as noted previously, prepared silicas with a range of

surface area (45 to 61 m^2/g). These were classified "active", "medium active" and "inactive" according to their effect on the physical properties of the respective vulcanizates. Interestingly, the "inactive" fillers could not be extracted by alkali from the filler-polymer gel at filler concentration below 40 volumes. The "active" silica could be extracted easily at lower loadings. Gel structure was reported to remain intact—ash free—after extraction and drying[131].

The mechanism of filler-polymer gel formation and the relation of this reaction to the properties of the subsequent vulcanizate have been objects of considerable research. Early investigators[132] realized that some relationships existed between surface area and bound rubber development. Their observations favored the concept, which became widely accepted, that bound rubber formation was due almost exclusively to adsorptive effects by carbon black fillers[121]. Experimental results with various fillers were obtained, however, which could not be explained solely on the basis of adsorption. For example, Graphon (surface area 85–100 m^2/g) is not consistent in its participation in carbon gel formation[133, 134]. It failed to conform to the usual surface area dependent relationship and the extent of crosslinking in its gel was low[135]. Similarly, fine particle calcium silicate (surface area 80 m^2/g) exhibits erratic behavior in bound rubber production, as compared to fillers of similar physical dimensions[73]. Endter[136] observed bound rubber formed with calcium silicate (surface area 40 m^2/g) under the electron microscope and found that it appeared loosely knit, resembling a polymer gel.

Not only have further difficulties been encountered in correlating the extent of bound rubber formation with surface area of fine particle fillers, but as Parkinson[137] observed in his recent monograph on reinforcement, the data from different workers on the relative magnitude of bound rubber for various fillers tend to be inconsistent. The experience of Endter and Westlinning[138] is typical. They prepared some experimental silicas which possessed physical characteristics such as surface area, particle size and distribution of particle size similar to Durosil. The degree of dispersion of the fillers in rubber and extent of bound rubber formation were reported equal to those obtained with the control Durosil mixtures. Yet, the bound rubber realized with the experimental silicas swelled only about one-third that of the gel produced by the control. Obviously, there were significant differences in the crosslink density between the Durosil rubber mixture and the filler-elastomer compositions containing the experimental silicas. The experimental silicas appear to be considerably more active than the Durosil in promoting crosslinking.

These observations and those noted previously in connection with fine particle calcium silicate can be explained by a consideration of the kinetics of network formation which show that incipient gel formation can occur with the addition of relatively few crosslinks. Hence, the absence or presence of a few crosslinks at the critical concentration would probably result in obtaining either no gel or an amount of gel close to the maximum obtainable at the filler concentration. Further crosslinking within the neighborhood of the filler particles would not result necessarily in more bound rubber. Boonstra and Dannenberg[82] also investigated the bound rubber-crosslink relationship. The data in Table XXX were abstracted from the report on the results of their research using SBR-1500. It appears, then, that a comparison of the magnitude of bound rubber production between fillers, without the consideration of at least the parameter of crosslink density, is of limited significance.

c. Evidence that bound rubber formation is a chemical reaction.—The adsorption theory also failed to account for the high temperature coefficient

TABLE XXX

BOUND RUBBER AND CROSSLINK DENSITIES FOR MILLED (120° F) FILLER–SBR 1500 MIXTURES AT 30 VOLUME LOADING

Filler	Bound rubber, % on polymer	Crosslink density of bound rubber matrix, moles/cc $\times 10^4$
Fumed silica	52.3	14.0
HAF black	33.4	5.0
EPC black	6.4	1.7
Precipitated silica	25.6	4.0
Precipitated calcium silicate	20.2	0.79

of the filler-polymer gel reaction[139]. Kraus and Dugone[135] calculated activation energies in the range 16–20 kcal for the thermal SBR-carbon reaction for four blacks. With Graphon, the reaction was not temperature dependent. Wagner and Sellers[140] reported the results of a similar study with HAF black, a fine particle silica and a coated silica in SBR and butyl, respectively. Their results are tabulated in Table XXXI. The information in Table XXXI, and that reported by Kraus and Dugone[135], supports the idea for the chemical nature of the bound rubber reaction. Further evidence is found in the well-known requirement of unsaturation in the elastomer[134].

It should be emphasized that adsorptive mechanisms are not considered entirely absent in the bound rubber phenomenon. The irreversibility of the adsorption of rubber from solvent/rubber mixtures onto blacks indicates, however, that purely physical effects are limited[135].

d. Nature of chemical reaction leading to bound rubber.—An oxidative process was early thought to be responsible for the thermal reaction forming bound rubber[141]. Rehner[142] was concerned about the possible significance of the effects reported by Menadue[130], especially since the effects seemed to depend on the nature of the fillers, none of which were recognized oxidizing agents or oxidation catalysts. He turned for an explanation to the well-known sensitivity of an unsaturated rubber under stress towards oxidation. Rehner reasoned that in the vicinity of the filler particle, the chains are in a highly stressed state. The magnitude of such stresses would depend on the presence of a filler sufficiently active to form a firm adherence to the rubber matrix. Enhanced oxidation under stress would involve crosslinking and/or scission in the elastomer. With a limited supply of oxygen, crosslinking would be expected to predominate. Thus in the vicinity of a filler particle, according to this concept, a rapid oxida-

TABLE XXXI

ACTIVATION ENERGY FOR FILLER–POLYMER INTERACTION

Filler	Polymer	ΔH, kcal/mole 105–190° C	ΔH, kcal/mole 60–140° C
HAF black[a]	Butyl	19	18
Fine particle silica[b]	Butyl	18	18
HAF black[a]	SBR-1500	18	18
Fine particle silica[b]	SBR-1500	17	17
Coated silica[c]	SBR-1500	—	15

[a] Philblack O.
[b] Hi-Sil 233.
[c] Valron Estersil.

tive crosslinking reaction would produce a gel. Such crosslinking would not necessarily involve the filler.

There is evidence that the carbon black surface, at least, would not be directly involved in the stoichiometry of an oxidizing reaction. Although the extent of the bound rubber formation is reported to depend[119, 121] on surface area (calculated from electron microscope measurements) for a wide variety of carbon blacks, it has been shown that these blacks exhibit large differences in the amounts of oxidative groups present on their surfaces[143]. Stickney[133] and his co-workers observed, however, that reinforcing carbon blacks exercise a catalytic effect on the oxidation of the iodide ion to iodine. This effect is surface area dependent, seems independent of the surface chemistry of the black, and requires the presence of molecular oxygen. Catalytic effects of carbon

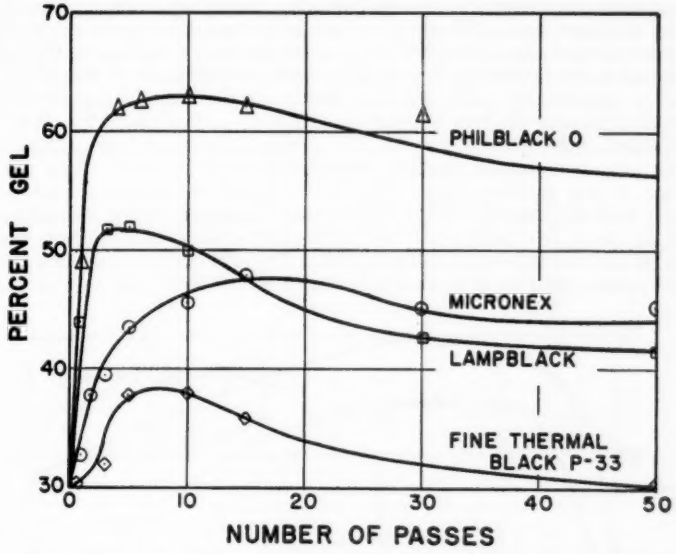


FIG. 20.—Variation of gel content with type of carbon black (data from Reference 148).

blacks and fine particle silicas in polymerization processes conducted at reasonable temperatures (50° C or below) are known[144–146].

The investigations of W. F. Watson and his colleagues further confirm the chemical nature of filler-polymer gel development. By the use of cold milling techniques, the reactive species involved were identified and a reaction mechanism proposed. Pike and Watson[147] concluded that during cold milling, rubber hydrocarbon chains rupture into free radicals and recombine or react with oxygen or other free radical acceptors. Elastomers with reduced unsaturation show considerably less tendency to react with acceptors, presumably because the unstabilized alkyl radicals recombine so speedily. This study was extended to include the action of fillers as acceptors of reactive polymer fragments formed on cold milling filler-polymer mixtures. Fillers were incorporated into the elastomer by a freeze-drying technique to avoid excess bound rubber

TABLE XXXII

EFFECT OF INHIBITORS ON BOUND RUBBER DEVELOPMENT ON COLD MILLING AN HAF (50 PHR)–NATURAL RUBBER MIXTURE

Inhibitor	Concentration of inhibitor, moles/gm $\times 10^4$	Max. bound rubber, %
None	—	66
Hydrazobenzene	1.87	50
Thiophenol	0.69	42
2,2-Diphenyl-picrylhydrazyl	0.16	32

development prior to milling. The freeze-drying technique involves dispersion of the fillers in a polymer-benzene mixture by ball milling, freezing the mixture and removing the solvent under reduced pressure. Small aliquots of the masterbatch were respectively passed through a cooled, tight mill for a specified number of passes each. Fller-polymer gel development, as measured by benzene insoluble polymer, passed through a maximum, depending on the filler. Additional passes resulted in less bound rubber, probably due to the effects of oxidative degradation exceeding the effects of the crosslinking processes. Figure 20 illustrates the results obtained with some carbon blacks[148]. With no filler present, little gel was formed. In further experiments, free radical acceptors were incorporated into the polymer-filler mixture at the time of ball milling. It was theorized that some of these reagents would compete successfully with the black for the polymer chain fragments created by milling to terminate them. In such cases the maximum network development, hence bound rubber, would be expected to be less. The effect of inhibitors in a HAF-natural rubber mixture is tabulated in Table XXXII[148]. The data in Table

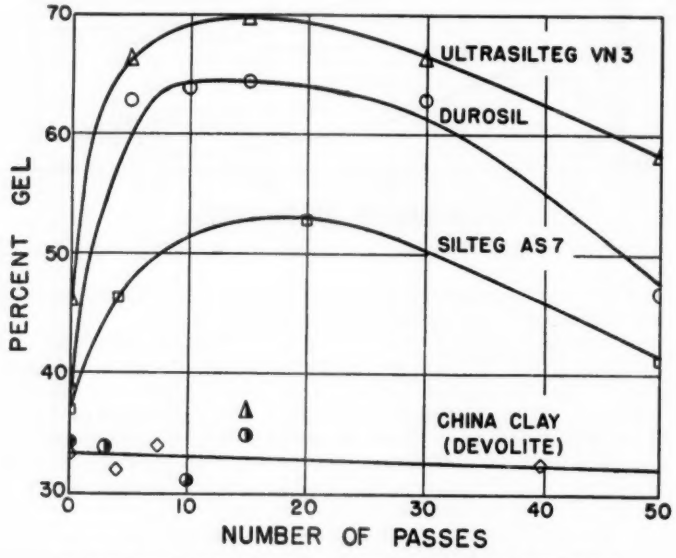


FIG. 21.—Variation of gel content with silicate fillers (data from Reference 149). △ Ultrasilteg VN3 and 1% thiophenol; ◑ Durosil and 1% thiophenol.

XXXII suggest that the filler and the organic free radical acceptors performed similar functions. Filler participation (no inhibitor) resulted in crosslink formation, while the chain stoppers competing with the filler prevented recombination, or combination of the free radicals of the chains with the filler.

Fine particle silicas and silicates were found to perform similarly to reinforcing carbon blacks, Figure 21[149]. Thiophenol reduced gel formation in the white mixtures to a similar extent as experienced with the carbon black masterbatches.

Several other fillers, considered to be semi-reinforcing, also gave on cold milling a reproducible increase in the amount of rubber, which was insoluble in benzene. Results by their use are compared in Table XXXIII to those obtained with Ultrasilteg VN3 and Philblack O[149].

The significance of the large quantities of bound rubber produced by the semi-active fillers is deceptive. Whereas the silica and black gels were well defined, the insoluble matter containing the other pigments failed to remain coherent on shaking. This illustrates again the importance of characterizing bound rubber in terms of network development, as well as quantity of gel.

TABLE XXXIII

MAXIMUM BOUND RUBBER DEVELOPMENT WITH VARIOUS FILLERS (50 PHR) IN NATURAL RUBBER DURING COLD MILLING

Filler	Gel, %
Ultrasilteg VN3	70
Philblack O	65
Activated magnesium carbonate	52
Activated calcium carbonate	51
Magnesia	49
Frantex B_1	45
Calsil	45

Wagner and Sellers[140] confirmed the observations of Watson in connection with gel formation on cold milling fine particle silica pigments in natural rubber.

From his work, Watson[148] also reported a drastic reduction of carbon black gel when unextracted pale crepe was used. He ascribed the effect to the presence of xylyl mercaptan or other efficient free radical acceptor used for bleaching the rubber. In some of the experiments of Wagner and Sellers investigating the comparative influences of carbon black and fine particle silica, unpurified pale crepe was used also. Results were obtained with carbon black similar to those reported by Watson. However, instead of the incoherent gel produced by the HAF black mixture, the silica masterbatch yielded significantly larger amounts of a tightly knit gel. This experience suggests that whatever the identity of the inhibitor, the silica apparently competed with it more successfully than the black for the sheared polymer chains.

The experimental results describing the formation of bound rubber on cold milling are consistent with the free radical mechanisms proposed by Watson;

$R—R \longrightarrow R^{\cdot} + R^{\cdot}$	Scission by shear forces yields allylic radicals or peroxidic $RO^{\cdot}$
$R^{\cdot} + R^{\cdot} \longrightarrow R—R$	Radical recombination
$R^{\cdot} + X \longrightarrow RX$	Termination by acceptor
$2R^{\cdot} + F \longrightarrow R—F—R$	Crosslinking by filler acceptor

Endter and Westlinning[138] protested the significance of Watson's findings on the mechanism of bound rubber formation. They found little filler-polymer gel existing immediately after milling. At least 20 minutes rest was required after milling before a coherent gel appeared. These findings have been verified by other investigators[150]. The delayed (up to 24 hours) effect generally is attributed to the time required for the disentanglement of radical fragments for subsequent reaction. The residual reaction was found to have a low order of activation energy, 7–8 Kcal[150].

In order to account for the requirement of polymer unsaturation in bound rubber development and reinforcement generally; for the different effects of various fillers; and for the continued development of bound rubber upon storage of Aerosil in natural rubber mixtures; Endter and Westlinning[138] proposed a polarization theory. According to this theory the double bond structures in the elastomer are polarized by surface forces on the filler. Filler-polymer and polymer-polymer linkages then occur by dipole-dipole interactions. Various other theories also have been suggested[130, 151] to account for filler action on an electrostatic basis. An alternative explanation that could be suggested for the continued gel formation upon storage of filler-polymer mixtures would involve crosslinks formed by radicals from peroxide decomposition. The elastomer would be peroxidized by slow reactions with dissolved oxygen. The

TABLE XXXIV

BOUND RUBBER DATA FOR SOME FILLERS IN NATURAL RUBBER AND SBR

Fillers	Bound rubber, %	
	Natural rubber	SBR
Pyrogenic silica (Aerosil)	70.9	49.6
ISAF black (Corax 6)	60.4	49.8
Channel black (CK 3)	53.2	35.6
Precipitated silica (Durosil)	49.2	21.9
Calcium silicate (Calsil)	33.9	6.0

polarization theory fails to explain the reduction of bound rubber with the use of SBR rubber, Table XXXIV[138]. A rubber containing such a highly polarizable substituent as a phenyl group would be expected by this theory to form more bound rubber.

Other investigators[152] found that any preferential adsorption of SBR from its solutions (xylene) by carbon black was not on the basis of the chemical composition of the polymer. Infrared studies showed that the phenyl content of the unadsorbed SBR fraction was unchanged from the original. Adsorption by carbon black under these conditions was sensitive mostly to molecular weight.

e. Structure of fillers permitting participation in bound rubber.—The accepted mechanism for bound rubber development requires chemical characteristics of a filler capable of accepting unpaired electrons. The surface chemistry of carbon black[143] as well as its internal structure [153, 154] offers interesting possibilities for carbon black to act as a radical acceptor of a special polyfunctional type. The chemistry of silica surfaces, however, has been studied less extensively in connection with the behavior as a reinforcing filler in elastomers. Wide differences in the comparative chemistry of the black and silica surfaces precludes, at present, any justification of the bound rubber reaction in terms of common surface groups. A consideration of the comparative structural char-

acteristics of silicas and siloxanes encouraged the proposal[140] of a structure for silica which would have features similar to that assumed present in carbon black. Because of resonance structures, atoms in carbon black and silica would be enveloped in an extensive cloud of π electrons. It would be expected that such a molecular orbital could accommodate a limited number of free electrons from radical fragments with little increase in energy. The acceptance by a filler particle of two or more fragments from different elastomer chains would create a crosslink. Support for this concept is found in the observed presence of unpaired electrons in carbon black[153, 154], the radical character of carbon black[155], and the ability claimed for silica, ground and stored under inert conditions, to retain its activity to react with ethylenic monomers for several days[156].

f. Direct influence of bound rubber on properties of vulcanizate.—The influence on vulcanizate properties, of fillers, or the effects of treatments of filler-polymer mixtures, often manifested first as bound rubber, seems convinc-

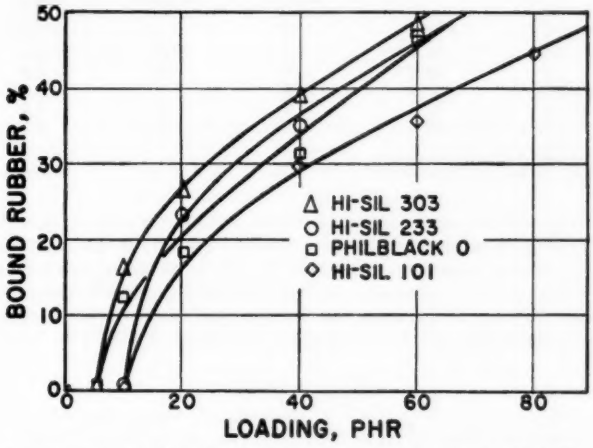


FIG. 22.—Variation of bound rubber with loading for silica and carbon black fillers (data from Reference 73).

ing. The mode of transmittal of these effects, however, remains obscure. There is good reason to believe that the formation of the actual gel may be incidental to the important effects passed on to the cured compound.

Manifestations in both bound rubber and vulcanizate resulting from the physical characteristics of the fillers seem obvious and will not be belabored. Parkinson[137] observed that since bound rubber (referring to that obtained with carbon black) is related to particle size (or surface area), correlation would be expected with such vulcanizate properties as rebound resilience, tear and abrasion resistance. He also held that the absence of a maximum in the increase in bound rubber with carbon black loading (similar behavior with reinforcing fine particle silicas, see Figure 22)[73] was inconsistent with an important relationship to reinforcement. He did not discuss the significance of network development in the matrix of filler-polymer gel.

Extensive evidence, discussed previously, suggests the existence of chemical factors inherent in specific fillers or specific filler-polymer mixtures which in-

fluence the nature of both the filler-polymer gel and the vulcanizate. Direct contributions by a mature network developed in the filler-polymer mixture are precluded by the plastic demands of the uncured stock. As shown by the results of the investigation of Boonstra and Dannenberg[82], crosslink development in bound rubber generally remains embryonic, Table XXXV.

The relatively large crosslink density reported by these investigators for the gel formed with anhydrous silica apparently also was observed by others.

TABLE XXXV

NUMBER OF CROSSLINKS IN VULCANIZED GRS–1500 AND IN THE BOUND RUBBER AT 30 VOLUME LOADINGS[a]

Filler	Filler-polymer gel: % on polymer	Filler-polymer gel: Crosslink density, moles/cc $\times 10^5$	Vulcanizate crosslink density moles/cc $\times 10^5$	% of vulcanizate[b] crosslink density contributed by crosslinks in bound rubber
EPC black	26.4	1.7	108	0.4
HAF black	33.4	5.0	91	1.8
Anhydrous silica	52.0	14.0	70	10.4
Hydrated silica	25.6	4.0	70	1.5
Calcium silicate	20.2	0.79	73	0.2

[a] Abstracted from Table in Reference 82.
[b] Calculated from data in Reference 82.

Scheele, Mau, and Kemme[157] found that the crosslink density in bound rubber formed on the cold milling (50° C) of Aerosil (5–10 phr) in natural rubber was sufficient to cause an erratic swelling behavior in the thiuram vulcanizates.

The failure of large differences in bound rubber produced in silica/natural rubber masterbatches to influence the development of network structure in the respective vulcanizates also has been observed, Table XXXVI[73].

TABLE XXXVI

THE INFLUENCE OF FILLER–POLYMER GEL ON CROSSLINK DEVELOPMENT IN 30 VOLUME HYDRATED SILICA–FILLED VULCANIZATES (AT OPTIMUM CURE)

Elastomer	Filler-polymer gel, % by wt. of polymer	Crosslink ratio* $\eta/\eta_0 \times 10^{-4}$
Natural rubber	55	0.6
	84	0.6
Butyl	9	0.8
	22	0.8
SBR	30	1.2
	84	1.1

* η and η_0 represent the crosslink density (equilibrium swelling) of filled vulcanizate and unfilled vulcanizate, respectively.

With no elastomer was there a measurable influence on the crosslink density caused by the varying amounts of gel developed prior to vulcanization. A similar effect was noted using HAF black in these elastomers.

The accumulated experience noted above prompts the suggestion that an important function performed by reinforcing fillers during milling could be a steric one. Their action would be to align polymer chains properly and suf-

ficiently close[158] in the vicinity of the filler, so as to encourage "reinforcement" interaction during vulcanization. Practical demands of such organizational[159, 160] influences would require the chemical and physical characteristics expected of a reinforcing filler. The dramatic consequences[161] on the properties of filled vulcanizates obtained by milling latex-compounded masterbatches, as well as those obtained by other latex processing techniques[162, 163] designed to improve the "wetting"[120, 109] of the polymer by the filler, seem to illustrate results of steric effects.

TABLE XXXVII

PROPERTIES OF AEROSIL (50 PHR) FILLED POLYBUTADIENE COMPOUNDS

Compound	A	B
Bound rubber, %	21.9	17.5
Properties of vulcanizate cured 50 minutes at 292° F		
Tensile strength, psi	450	2120
Elongation, %	200	620
Hardness, Shore A	87	73
Abrasion index	46	147
TR 70, ° C	+5	−34

Influences noted above which are exerted by reinforcing fillers on the vulcanizate are the result of localized[164] effects. Any practical consequences in the vulcanizate, of filler characteristics recognized during bound rubber development, probably would not be independent of the more general influences of the filler on the vulcanization process. Obviously, a reinforcing potential suggested in these terms for a filler could be obscured by a malfunctioning curing system. A typical example has been reported[119] with the use of Aerosil cured in different formulations, Table XXXVII.

The bound rubber values are similar and promising for both "A" and "B" stocks listed in Table XXXVII. A realization of the indicated reinforcing

TABLE XXXVIII

COMPOUND FORMULATIONS

Formulation, basis 100 parts polybutadiene and 50 parts Aerosil

Compound	A	B
Zinc oxide	1.5	5
Sulfur	2.0	3
Stearic acid	—	3
Piccolite S-100	—	10
Diethylene glycol	—	3
MBTS	1.5	—
MBT	—	1.2
Methyl tuads	—	0.15

potential, however, was affected drastically by the choice of formulation "A", used by these investigators for evaluating blacks; or by the use of formulation "B" used for Aerosil on the basis of formulations suggested for use with a coarser hydrated silica, Table XXXVIII.

Thus, the phenomenon of bound rubber might be considered as a preview of the reinforcement potential of a filler. A realization of any indicated potential, in terms of vulcanizate properties, depends upon the development of a curing system fully functional with the specific filler and elastomer.

E. PARTICIPATION OF FINE PARTICLE SILICAS AND SILICATES IN VULCANIZATION–REINFORCEMENT REACTIONS

Reinforcement appears to be a function not only of the physical characteristics of a filler and of ill-defined chemical factors apparent at the time of mixing of filler and polymer, but also the extent to which a filler influences the vulcanization reaction. In the following discussion of attempts at the evaluation of the latter influence, it will be found that crosslinking data has been relied upon extensively. Most of the information reported was obtained by equilibrium swelling measurements[69, 165]. This procedure is not only convenient[60, 66, 67, 166], but the results can be verified by the more tedious method involving equilibrium modulus[167]. The heavy reliance on crosslink data, even considering their limitations in significance, can be defended logically[67]. On an *a priori* basis, changes in the physical properties of vulcanizates must have their origin in the quantitative and qualitative changes accompanying network development during cure. Knowledge at present on the qualitative nature of crosslinks is extremely limited, of course. Often, however, information supplementing that furnished by crosslink measurements is available where qualitative implications are possible.

1. *Performance of fine particle silica and silicate fillers in peroxide cures.*— It seems reasonable to attempt a confirmation of any indicated reinforcing po-

TABLE XXXIX

PHYSICAL PROPERTIES

t-butyl perbenzoate (4.1 phr) vulcanized, calcium silicate filled (25 phr) natural rubber compound

Unaged			Aged 14 days at 70° C		
Tensile psi	300% Modulus psi	Elong. %	Tensile psi	300% Modulus psi	Elong. %
1990	240	648	1800	313	575

tential by evaluation in a curing system characterized by simplicity. Such a curing system should not be inhibited by the filler. On this basis, vulcanization by peroxide becomes a candidate.

A treatment of the use of fine particle silica and silicate fillers in a peroxide curing system must include the pioneer work of Braden, Fletcher, and McSweeney[168]. These investigators evaluated t-butyl perbenzoate and 2,2-di(t-butylperoxy)butane as curing agents for natural rubber compounds filled with a calcium silicate of unspecified properties. With added antioxidant, these vulcanizates exhibited good properties, normal and aged, Table XXXIX.

More recently dicumyl peroxide (Di-cup)[169] has become available as a curing agent. Decomposition of dicumyl peroxide in the presence of fillers, which are not strongly acid, would be expected to initiate crosslinking by an uncomplicated free radical mechanism[166]. Thus, the similarity to the presently accepted mechanism of bound rubber formation, in which silica participated so well, should simplify the evaluation process. The results of an investigation of the use of silica in Di-cup curing system are summarized in Table XL[73].

The significance of "filler participation", η/η_0, the ratio of the number of crosslinks formed in the filled compound per gram of elastomer, to the number of crosslinks formed in the unfilled vulcanizate per gram of elastomer, can be obscure. As also used by Kraus[67], who employed the term to suggest "filler

TABLE XL

DEVELOPMENT OF CROSSLINKS IN A NATURAL RUBBER–SILICA (50 PHR) DICUMYL PEROXIDE COMPOUND

Optimum cure at 307° F[a]

Filler	Crosslink density moles/g $\times 10^4$	η/η_0[b]
None	0.6	—
Hi-Sil 233	0.9	1.5
Hi-Sil 101	1.1	1.8

[a] Recipe: Natural rubber, 100; Di-cup, 1.8.
[b] Ratio: Crosslinks filled compound/crosslinks unfilled compound.

contribution", the η/η_0 ratio, here, is understood to designate not only the extent of the contribution of any filler-polymer linkages, but also the additional crosslinks formed in the filled vulcanizate due to any catalytic effect of the filler on the curing reaction. The two effects are seldom independent. An interpretation of the significance of the η/η_0 ratio in terms of filler-polymer interaction obviously requires an estimation of effects on cure by the filler.

The effects of the filler on the vulcanization reaction can be minor. Working with silica-filled silicone rubbers crosslinked with peroxides, Bueche[112] made some quantitative estimates of the relative contributions of filler and peroxide to the total network structure. He derived Equation (20) which demands that the crosslinking efficiency of the peroxide be independent of the filler concentration.

$$C_f = N_0(\alpha^1 - \beta/C_0) \tag{20}$$

Here C_f is the number of moles of crosslinks contributed by the filler per gram of rubber, C_0 is the number of crosslinks per gram of gum in the absence of those

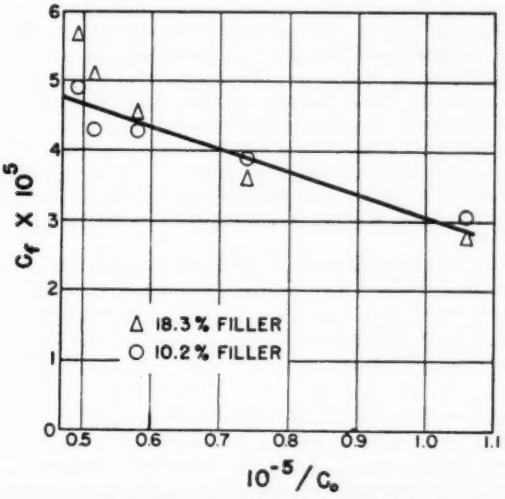


FIG. 23.—Apparent number of moles of crosslinks contributed by the filler vs. reciprocal of the crosslinks introduced by the peroxide (data from Reference 112).

from the filler, α' and β are constants for a given polymer-filler system, and N_0 is the number of moles of polymer per gram of gum that have been adsorbed on the filler. The contribution of the filler to the total crosslinks was estimated by subtracting the crosslink level of the gum from that of the filled vulcanizate. These values were plotted against the reciprocal of the crosslink concentration in the gum stock, $1/C_0$, Figure 23. The good agreement with the original premise indicates not only the independence of peroxide efficiency with filler concentration, but that filler-polymer linkages become effective on demand of the curing system, i.e., the contribution of crosslinking by the filler depends on the degree of crosslinking of the sample. Here C_f, crosslinks contributed by the filler, account for 85% of the increase in total crosslinks.

Sometimes the influence of the filler is a subtle one. In their detailed study of peroxide-crosslinked, black-filled polyethylene, Dannenberg and coworkers[166] took extreme care to confirm that basic carbon blacks do not interfere with the normal free radical decomposition of dicumyl peroxide. Yet, these blacks exercised some retardation of cure at lower temperatures. This was ascribed to restrictions on the movements of polymer radical chains by the filler and combination of the filler with some of the polymer chains.

Referring again to Table XL, the two silicas changed, respectively, an apparent filler contributed increase of 50 and 80% in the total crosslink density of the vulcanizate. Kraus[67] reported an increase in crosslink density of 20% for an HAF (50 phr)/SBR 1500 vulcanizate crosslinked with dicumyl peroxide. The contribution found by Kraus is considerably less than that usually found by HAF blacks in sulfur-cured stocks.

The relative increase in the apparent filler contribution obtained with the use of Hi-Sil 101, Table XL, probably reflects the more basic nature of this filler. Hi-Sil 101 (pH 9.0) would have a lesser number of acidic sites on its surface than Hi-Sil 233 (pH 7.0). Dicumyl peroxide can decompose by an ionic mechanism under acid conditions[170]. To the extent that this occurs, products are produced which would not initiate crosslinking.

2. *Performance of fine particle silica and silicate fillers in radiation cures.*— Vulcanization by radiation offers another opportunity to confirm the idea suggested by bound rubber performance that fine particle silica can contribute in a significant manner to the vulcanization-reinforcement reaction. The initial reactions, resulting from exposure of elastomers to high energy radiation, which culminate in the production of free radical fragments, are more complicated than those observed with the use of peroxides[158]. Crosslinking in high polymers, occurring upon exposure to radiation, is similar to the reaction in the presence of peroxides[95], in that it is assumed to proceed by a free radical mechanism[171–173].

Exposure of natural rubber-silica mixtures to high energy radiation confirmed the results observed in peroxide crosslinked silica-filled vulcanizates. In the radiation study, as in the peroxide work, a high degree of participation of silica in the vulcanization-reinforcement reaction, as evidenced by η/η_0 values, was observed[92]. Some results of this investigation are summarized in Table XLI.

An inspection of the results in Table XLI shows that the η/η_0 values for the black vulcanizates are similar whether radiation or sulfur cured. The radiation-cured silica compounds, however, exhibited considerably higher η/η_0 values than those found for the respective filled sulfur vulcanizates. Significant participation of the silica is evidenced by the increasing of η/η_0 ratios with

TABLE XLI

COMPARISON OF FILLED NATURAL RUBBER COMPOUNDS CROSSLINKED BY RADIATION AND BY SULFUR CURATIVES

Filler	Loading, phr	Radiation cure: Dose, MR[d]	Radiation cure: η/η_0	Sulfur cure[a]: at 287° F min	Sulfur cure[a]: η/η_0
Fine particle hydrated silica[b]	29.3 (15 vol.)	40	2.2	15	1.1
		80	2.0	30	1.1
Fine particle hydrated silica[b]	58.5 (30 vol.)	40	3.8	15	1.0
		80	3.6	30	1.1
HAF black[c]	54.0 (30 vol.)	40	2.1	15	1.9
		80	2.3	30	1.9

[a] No. 1-RSS, 100; filler, as indicated; Antioxidant 2246, 1.0; MBTS, 0.8; DOTG, 1.2; triethanolamine, 2.0; sulfur, 3.0; stearic acid, 3.0; zinc oxide, 5.0.
[b] Hi-Sil 233.
[c] Philblack O.
[d] Megarep.

loading; 2.1 at 15 vol. to 3.7 at 30 vol. Experimentally, it was reassuring that the η/η_0 ratios changed little with increasing dose for either filler.

The incorporation of 2 phr of a sterically-hindered phenolic antioxidant (Antioxidant 2246) reduced the crosslink density in the unfilled, as well as silica-filled irradiated stocks, by about 50%. The η/η_0 value, then, was the same as for the stocks without antioxidant. The uniformity of action on the gum, as well as silica-filled compounds by free radical acceptor, suggests that the apparent participation of the filler in the vulcanization reinforcing reaction cannot be attributed to a different mechanism of crosslinking induced by this filler[145]. It is interesting to note that the crosslinks in the sulfur-cured stocks were reduced only 10–15% by the incorporation of an additional 2 phr of antioxidant.

Crosslinking by the radiation of siloxane elastomers also occurs by a free radical mechanism. In this polymer the structure of 75% of the crosslinks could be confirmed by infrared measurements[174], and because they were free from residues which accompany peroxide vulcanizations, radiation crosslinked polydimethylsiloxanes showed no stress relaxation[175].

TABLE XLII

BEHAVIOR ON AGING OF PEROXIDE AND RADIATION-CURED SILICONE RUBBERS

Vulcanization agent	Peroxide	Radiation	Radiation
Filler	Anhydrous silica	Anhydrous Silica	Black
Tensile strength, psi			
Unaged	1088	876	787
Aged (24 hrs/250° C)	1045	672	542
Elongation, %			
Unaged	587	580	435
Aged	369	486	115
Shore Hardness			
Unaged	41	29	35
Aged	55	26	75

Warrick[176] confirmed the excellent aging properties for the irradiated silica-filled silicone rubber, which might have been predicted by the stress relaxation measurements on the gum stock[175]. He reported some interesting differences in the behavior of black and silica-filled radiation crosslinked rubbers. Different physical properties also were observed between the benzoyl peroxide and radiation-cured silica compounds. The results of Warrick's[176] investigation are summarized in Table XLII.

A patent issued to General Electric[177] confirms the advantage of silica in radiation-cured silicones, Table XLIII.

TABLE XLIII

VULCANIZATION OF FILLED SILICONES BY RADIATION (2 MR)

Filler	Tensile (kg/cm²)
45 phr silica	63.6
50 phr black	31.9

Jackson and Hale[178] reported on the physical properties of Philblack A and Silene EF loaded natural rubber and SBR cured by radiation. Advantages in aging were revealed for the silicate-filled compounds.

3. *Performance of fine particle silica fillers in sulfur cures.*

a. Influence on sulfur vulcanization attributed to adsorption effects of fine particle silica fillers.—The behavior of fine particle silica and silicate fillers in sulfur-cured vulcanizates of unsaturated polymers has been the object of many compounding studies[49, 50, 52, 136, 179, 180]. In few of these has the elucidation of structural parameters been a major objective. Information did emerge, however, that silica-filled vulcanizates required larger amounts of curatives than did black vulcanizates in order to achieve practical properties. Further in-

TABLE XLIV

EFFECT OF INCREASED ACCELERATION ON THE DEVELOPMENT OF CROSSLINKS AND EFFICIENT UTILIZATION OF SULFUR IN SILICA VULCANIZATES[a]

Sulfur, phr	Santocure[b], phr	$\left[\frac{S}{\eta'}\right]^c$ in vulcanizate	
		Gum	Silica filled
1.75	1.5	5.4	7.8
1.75	3.0	4.8	4.8

[a] Formulation: SBR 1500, 100; Hi-Sil 101, 50; zinc oxide, 5; stearic acid, 2; phenyl-2-naphthylamine, 1.5.

[b] N-cyclohexyl-2-benzothiazolesulfenamide, Monsanto Chemical Company.

[c] Moles of sulfur combined per moles of crosslink formed in one cc rubber. For comparison with other data $\eta' = \eta \times$ density of rubber.

vestigations[67], which also disclosed structural effects, suggested mechanistic reasons for the effects on the usual stress strain properties. Such effects generally are dismissed as being due to delayed cure. In the formulations employed by Kraus[67], the delayed cure effects observed at lower acceleration cannot be explained on the basis of reduction in combined sulfur. Over 96% of the sulfur was combined in the cures reported. As the data in Table XLIV reveal, an increase in accelerator level was reflected in an increase in crosslink density. Thus, a decrease in S/η' (moles sulfur/moles crosslinks) occurs.

An inspection of the data in Table XLIV shows that at both accelerator

levels sulfur is used at its maximum efficiency in producing crosslinks in the gum stock. The introduction of silica did not disturb the extent to which sulfur disappeared, but interfered with the conversion of sulfur into a useful entity, crosslinks. On the basis of these results, it appears that high volume loadings of silica interrupt some sequence of the reactions in which the accelerator participates to convert the combined sulfur into crosslinks.

Endter and Westlinning[136] insist there is little justification for blaming accelerator adsorption effects for delayed cures experienced with the use of high volume loadings of silica. These investigators worked with the same type of accelerator as Kraus[67]. They found that by deliberately depositing half of the accelerator on the surface of Aerosil, the accelerator requirements of the mixture actually could be reduced. Sulfur requirements could be reduced similarly.

Wolf[181] confirmed the experimental observations of Endter and Westlinning in his work with 2-mercaptobenzothiazoledisulfide (MBTS) and di-o-tolylguanidine (DOTG), but found them incomplete. He noted that depositing half of the MBTS (0.4 phr) on the silica and adding the remainder (0.4 phr)

TABLE XLV

ADSORPTION EFFECTS OF FILLER (60 PHR) ON MBTS AND DOTG IN NATURAL RUBBER VULCANIZATES

Disposition of accelerators		Cure 45 min. at 287° F	
MBTS added	DOTG added	300% Modulus, psi	Hardness, Shore
Normal mixing	Normal mixing	1110	79
½ on filler and ½ with normal mixing	Normal mixing	1010	70
All on filler	Normal mixing	670	65
Normal mixing	½ on filler and ½ with normal mixing	1020	72
Normal mixing	All on filler	1130	70
All on filler	All on filler	670	64

with the DOTG (1.2 phr) while mixing with the rubber, no significant change in physical properties could be discerned. This result can be explained in the same way as that reported by the workers with the sulfenamide accelerator. Sufficient accelerator remained in the compound, or could diffuse to it from the filler, to effect a satisfactory cure. On the other hand, when Wolf deposited all of the MBTS (0.8 phr) on the filler prior to mixing with DOTG and the other compounding ingredients, a sharp fall in the rate of cure occurred. In the case of DOTG, similar physical properties were obtained regardless whether the accelerator was added on the filler or in the normal way. Placing both accelerators (MBTS and DOTG) on the filler reduced the rate of vulcanization, thus reflecting the loss of MBTS. The results are summarized in Table XLV.

The data cited suggest that adsorption effects on the vulcanization-reinforcement reaction by reinforcing grade silicas are not negligible. Additional information obtained *in vitro* is irresistable in its support of the evidence. The large BET surface areas, in relation to their electron microscope diameters, suggest additional sites for selective adsorption of small molecules by silica

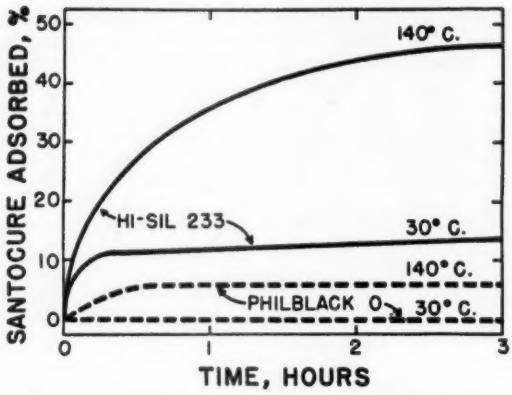


FIG. 24.—Adsorption isotherms for Santocure on Hi-Sil 233 and Philblack O (data from Reference 73).

fillers. Surface OH groups on silica possess acid properties and are important in the adsorption of molecules such as heterocyclics containing electron donor groups like oxygen or nitrogen[182] (also see Section IV—D). Vulcanization accelerators now commercially used qualify easily.

At temperatures from 30–140° C, fine particle silica removes N-cyclohexyl-2-benzothiazolesulfenamide (Santocure) from solution in xylene at a significantly higher rate than does HAF black, Figure 24[183].

The magnitude of the selectivity for adsorption of donor type accelerators as diphenylguanidine (DPG) by various fillers is shown in Table XLVI[184].

These data show the massive effect of BET surface area in promoting adsorption of the accelerator from benzene. The higher density of polar OH groups in the surface is held responsible for the greater adsorption of DPG by calcium silicate as compared to EPC black, despite the greater available surface area for the black. Beebe and his colleagues[100] observed the effects of increasing polarity of carbon black surface on DPG adsorption. In the series of blacks with decreasing amounts of oxygen on the surface, DPG adsorption decreased in the order MPC black (7.6 mg/g), MPC black heated to 927° C (1.1mg/g), and MPC black partially graphitized (Graphon) at 3200° C (0.8 mg/g).

Andresen[186] could find correlations only with pH of the filler in his investigations of the adsorption of DPG and MBT, respectively, on a number of blacks

TABLE XLVI

AVAILABLE SURFACE AREA AND DPG ADSORPTION BY VARIOUS FINE PARTICLE FILLERS FROM BENZENE

Filler	Surface area, m²/g		DPG adsorption,[b] mg/g pigment
	BET	E.M.[a]	
Anhydrous silica	188	160	49
Hydrated silica	150	124	45
Calcium silicate	80	95	21
HAF black	80	94	7
EPC black	110	100	11

[a] Calculated from average particle diameters determined by electron microscope observation.
[b] Procedure similar to that described in Reference 185.

and fine particle silicas. Adsorptions, however, were from polar solvents, ethanol or methanol.

Adsorption measurements made from solutions containing rubber might be more useful (and more difficult). In his widely misquoted article, Barron[160] found that the presence of rubber reduced the adsorption by carbon black of phenol from a benzene-water mixture.

Apparently the results of preferential adsorption studies conducted outside of the vulcanizate must be interpreted with caution. As noted previously, the effects of MBTS adsorption on the filler were real. Conversely, vulcanizate properties revealed little, if any, consequences of the total DOTG adsorption on the silica. Much of the reported[49, 187, 243] improvement in properties of silica-filled compounds obtained by the use of glycols may be due to influences on the adsorption of curatives or reaction intermediates.

Adsorption of another type in connection with silica has been demonstrated. Brooks and coworkers[90] stirred a mixture of silica, zinc stearate and benzene for a few minutes and then centrifuged. Examination of the supernatant benzene revealed that 85% of the zinc had disappeared. The stearic acid

TABLE XLVII

FORMATION OF ZnS AT VARIOUS FILLER LOADINGS*

Filler	$\frac{\text{Moles ZnS formed}}{\text{Moles ZnO consumed}} \times 100$		
	7.5 Min. cure	30 Min. cure	120 Min. cure
None	88	70	75
20 phr silica	77	67	67
50 phr silica	24	39	46
20 phr black	82	73	71
50 phr black	65	64	71

* Formulation: Natural rubber, 100; zinc oxide, 5; sulfur, 3; MBTS, 0.8; DOTG, 1.2; triethanolamine, 1.0; stearic acid, 3; filler as noted.

remained. No zinc was reported removed in similar experiments conducted in the presence of carbon black. Apparently, under these conditions zinc is adsorbed by silica as an ion. The well-known requirements of silica vulcanizates for larger amounts of zinc oxide may be accounted for on this basis[49]. Conducted at room temperature, the reaction of silica in benzene with zinc stearate must be a fast one. Measurements of the consumption of zinc oxide with time of cure in filled vulcanizates uncovered no evidence of any selective influence of black or silica (or loading of either) on the rate of zinc oxide disappearance[188]. The disappearance of zinc oxide was found to be a function of cure time.

The observations of Brooks and others can be reconciled with this experimental result by assuming that stearic acid acts as a stable zinc oxide solubilizer. From the soluble form, zinc can be adsorbed or utilized in the cure reaction sequence. Freed stearic acid then can react with more metal oxide and the process repeated[189]. Any adsorption of zinc, which reduces the amount available for the vulcanization reaction, would be expected to reduce or change the nature of crosslinking, Table XLVII[188].

Further implications of the reduction in zinc sulfide content of the more

highly filled zinc vulcanizates will be discussed in the next section covering the influence of fillers on the vulcanization-reinforcement reaction.

The results of the investigations of Stearns and Johnson[76] illustrates the hazards of evaluating the performance of silica in vulcanizates crosslinked with an incomplete curing system. They evaluated fillers on the basis of the response in a work function which was largely dependent on the extent of differences in crosslink density between the filled and unfilled vulcanizates. As indicated by the information in Table XLVIII, the procedure fails for silica stocks in the curing system employed.

The formulations used in both investigations, the results of which are tabulated in Table XLVIII, would be expected to yield about the same level of maximum crosslinks. It seems valid, then, to utilize the swelling data of Kraus to compare the relative network development to be expected in the silica and black compounds of Stearns and Johnson. From the data in Table XLVIII it is apparent that the vulcanizate containing silica possessed 28% less total crosslinks than the cured, unfilled compound. Loading with EPC, however, increased the total crosslinks by 40%. It is not surprising that with this formulation, the thermodynamic procedure adapted by Stearns and Johnson could find no reinforcement increment contributed by silica.

TABLE XLVIII

CROSSLINK DEVELOPMENT IN FINE PARTICLE SILICA AND EPC BLACK SBR VULCANIZATES

	Stearns and Johnson[a]	Kraus[b] (50 phr)	
	Silica and EPC Black (45 phr)	Silica	EPC black
I. Curing system			
Sulfur	2.0	1.75	1.75
Santocure	1.5	1.5	1.1
Zinc oxide	3.0	5.0	3.0
II. Crosslink density, moles/cc $\times 10^4$			
Unfilled vulcanizate, η'_0	—	3.40	2.36
Filled vulcanizate, η'	—	2.46	3.34
III. Filler participation in vulcanization reinforcement reaction as indicated by η'/η'_0 ratio	—	0.72	1.4

[a] Reference 76.
[b] Reference 67.

b. Influence of fine particle silicas on the course of the vulcanization-reinforcement reaction in sulfur vulcanization.—Catalytic activity of Aerosil in a tetraethylthiuram disulfide cure has been reported[157]. It was stated that its presence at 5 to 10 phr significantly increased the rate constants for the formation of zinc diethyldithiocarbamate. At this loading level and in the usual sulfur curing systems, reinforcing grade carbon blacks and fine particle hydrated silicas are characterized more by causing an increase in crosslinks than in any pronounced effect on rate of cure. This is shown by the data tabulated in Table XLIX[73].

For reasons pointed out in the previous section on adsorption effects, silica requires more curatives at the higher (30 vol.) loadings. As employed in the

TABLE XLIX

EFFECT OF FILLERS ON THE DEVELOPMENT OF CROSSLINKS IN NATURAL RUBBER VULCANIZATES

	η, moles/g rubber $\times 10^4$					
	Silica[a], phr			HAF black[b], phr		
	0	5	10	0	5	10
I. Crosslink development						
Cure, min at 307° F						
15	1.14	1.18	1.24	0.01	0.03	0.39
30	1.17	1.22	1.29	0.67	0.71	0.79
45	1.19	1.24	1.30	0.72	0.79	0.80
60	1.18	1.24	1.29	0.69	0.76	0.77
90	1.16	1.22	1.24	0.64	0.71	0.73
II. η/η_0 at maximum crosslinks						
Cure, 45 min at 307° F	—	1.04	10.8	—	1.09	1.11

[a] Natural rubber, 100; sulfur, 3.0; MBTS, 0.8; DOTG, 1.2; zinc oxide, 5.0; stearic acid, 3.0; triethanolamine, 1.0; Flexamine, 1.0; PBNA, 1.0; Hi-Sil 233, as shown.

[b] Natural rubber, 100; sulfur, 2.5; Santocure, 0.6; zinc oxide, 5.0; stearic acid, 3.0; Flexamine, 1.0; Paraflux 2016, 3.0; PBNA, 1.0; Philblack O, as shown.

gum control and with the low loadings cited in Table XLIX, these excess curatives effect the higher crosslink levels shown in the silica column. Despite the difference in crosslink levels, the two fillers enhanced the network development, as judged by the η/η_0 ratios, to about the same extent. Significantly the value of the ratio increased with the loading.

At more practical loadings, however, in the curing system employed to obtain the data listed in Table LXIX, silica fails to increase the value of η/η_0. Since, as demonstrated by Kraus[67], reinforcing carbon blacks, like HAF black, continue to increase the η/η_0 ratio with loading, it becomes apparent that silica is affecting the vulcanization process in some deleterious manner.

Reduced efficiency in the utilization of zinc oxide by silica to form zinc sulfide was indicated previously, Table XLVII. Confirmation is presented by the data in Table L, which show the reduction in zinc sulfide with increased loading despite the maintenance of high sulfur consumption[73]. The results of the examination of carbon black (HAF) vulcanizates are included for comparison.

A complete discussion of the implications of all the data in Table L is beyond the scope of this review. Considering the accompanying information, however, the contrast of the changes in zinc sulfide production seem sufficiently provoca-

TABLE L

CHANGES IN CROSSLINK DENSITY, COMBINED SULFUR, AND ZINC SULFIDE PRODUCTION WITH LOADING OF FILLER

	Silica*			HAF Black*		
Loading, phr	Maximum η moles/g $\times 10^4$	Sulfur combined, %	ZnS moles/g $\times 10^4$	Maximum η moles/g $\times 10^4$	Sulfur combined, %	ZnS moles/g $\times 10^4$
0	1.19	98	2.6	0.72	84	1.4
5	1.24	98	2.5	0.79	84	1.5
10	1.30	98	2.4	0.80	87	1.6
20	1.30	97	2.2	0.96	88	1.5
40	1.21	92	1.7	1.22	88	1.6
60	0.60	66	1.1	1.54	89	1.7

* Same formulations as Table XLIX.

tive to prompt comment. The appearance of zinc sulfide has been reported repeatedly to be connected with the participation of combined[189] sulfur in crosslink formation[190–192]. As shown in Table L, the silica curves tend to exhibit higher zinc sulfide values, at a given crosslink level, than the black counterparts. This may be partly a responsibility of the guanidine curing system[192]. Particular attention is directed to the constancy of combined sulfur and zinc sulfide values in the black stocks with increased loading, despite large increases in crosslink density. The creation of additional crosslinks which does not involve sulfur seems indicated here—at least which do not involve it in the manner that evolves zinc sulfide as a by-product. Some formation of C—C polymer, and filler-polymer linkages is suggested. Conversely, the decline in both crosslink

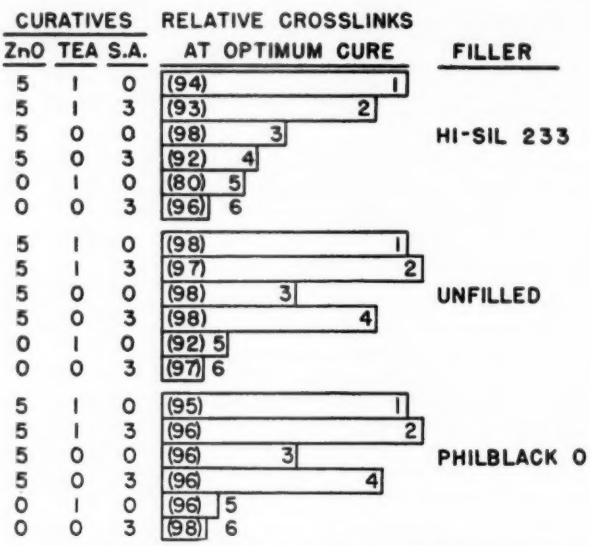


FIG. 25.—Effect of curatives on the development of maximum crosslinks in natural rubber vulcanizates using Altax-DOTG acceleration (data from Reference 73). The numbers in parentheses refer to per cent sulfur which has combined.

density and zinc sulfide content at higher silica loadings is additional evidence for interference by the silica in the vulcanization-reinforcing reaction.

An investigation of the action of various curatives in silica vulcanizates as affecting crosslink development was undertaken in the Columbia-Southern Research Laboratories. A summary of the results conducted with extracted natural rubber is depicted in Figure 25. In this Figure the distribution of curative variables (zinc oxide, triethanolamine (TEA) and stearic acid) is presented in the same order, vertically, for each bar graph A, B and C. The length of the bars is proportional to the maximum crosslink development for each stock. The series is normalized so that bar 1 in each graph is the same length.

The profiles in Figure 25 reveal the similarities and contrasts in the response of the silica and the black (or unfilled) vulcanizates to the action of curatives.

All reflect the low network development in the absence of zinc oxide (bars 5 and 6) and the greater activation effect of TEA over stearic acid even at this reduced crosslink level. The addition of zinc oxide (bar 3) about doubles the conversion of combined sulfur into crosslinks. This action probably reflects some solvating effect of DOTG.

Combining stearic acid with zinc oxide gives contrasting effects between the silica vulcanizates and the unfilled or black stocks (compare bars 3 and 4). With silica a drastic reduction in crosslinks occurs. The traditional[193] beneficial action of zinc oxide with stearic acid is observed in the other two stocks.

Adding TEA to the zinc oxide and stearic acid combination benefits all three stocks, but percentagewise, the silica compounds benefited most (compare bars 4 and 2). The silica vulcanizate improves even more by the omission of stearic acid with the retention of TEA (bars 1 and 2). Crosslinks reach their highest development here for the silica compound. Omitting stearic acid in favor of TEA decreases crosslinking in the black and unfilled stocks. As noted above, in the absence of zinc oxide, TEA had more of an accelerating effect on all compounds than did stearic acid (bars 5 and 6).

A consideration of these observations suggests that the influence of silica is large and specific. Subsequent inhibition of cure can be overcome only parti-

TABLE LI

REPLACEMENT OF ZINC OXIDE BY LITHARGE IN SILICA FILLED NATURAL RUBBER VULCANIZATES [a]

Filler Volume Loading	η[b] moles/g $\times 10^4$	η/η_0	PbS, moles/g $\times 10^4$
15	1.19	1.4	2.9
30	1.47	1.7	3.0

[a] Formulation: Natural rubber, 100; phenyl-2-naphthylamine, 1; stearic acid, 3; sulfur, 2.5; litharge, 10; MBTS, 1; selenium diethyldithiocarbamate, 0.2; Hi-Sil 233, as shown; (95% of sulfur combined).
[b] By equilibrium swelling at maximum crosslinks.

ally by means of an increase in the amount of zinc oxide[49]. Further practical improvements are realized by the use of TEA. Zinc oxide must be in soluble form to be useful in vulcanization[194]. As shown by bar 3 in the graphs of Figure 25, there was insufficient solubilization of zinc oxide in the absence of TEA or stearic acid to effect practical vulcanization in any stock.

Natural rubber contains about 3% fatty acids[195]. Processing requirements apparently demand an equal additional amount. Thus, in practical compounding with fine particle silica in the presence of thiazole-guanidine acceleration, the use of reagents similar to TEA seems mandatory.

The foregoing analysis of the response of curatives in the presence of silica pigments was confined to the thiazole-guanidine acceleration system in natural rubber. Conclusions from this investigation cannot be extended, necessarily, to predict the influence of silica fillers in other polymers or curing systems.

c. Examples of high silica participation in the sulfur vulcanization-reinforcement reaction as evidenced by high values of the η/η_0 ratio.—As indicated previously, the important characteristic of the peroxide and radiation curing systems is the absence of obvious retarding effects caused by silica fillers. From their investigations on the relative merits of radiation and present sulfur curing systems used to prepare silica filler natural rubber and SBR vulcanizates, Arnold, Kraus, and Anderson[196] recently observed that the full reinforcing potential of these fillers may not be realized in sulfur systems because of their inhibitory effect on cure.

An analysis of the influences effecting the efficient utilization of one component of the sulfur curing system, zinc oxide, encouraged its replacement with litharge[227]. The results are tabulated in Table LI.

A comparison of the η/η_0 values given in Table LI with those listed in Tables XLI and XLVIII, reveals that the use of litharge in the experimental compound caused significant increase in the apparent filler contribution by the silica. The crosslink value, η, did not decrease at practical loadings of filler as in MBT-guanidine-zinc oxide formulations (refer to Table L). Lead sulfide values reflect a constancy similar to that found for zinc sulfide in practical HAF filled vulcanizates (Table L).

It is concluded from the data in Table LI that in the experimental sulfur curing system, fine particle silica again exhibits a reinforcing potential suggested in its behavior in bound rubber development, peroxide cures and radiation cures.

VI. COATED SILICAS

The coating of fine particle silica or silicate fillers has been reported to improve performance in various elastomeric applications. Precedent is available for the adjunct activity given silicas in other applications by coating. Two similar applications are briefly cited here. Reinforced polyesters are reported to show enhanced properties if the fiber glass is treated with a specific coating prior to mixing and curing of the mixture[197]. Fine particle silica fillers, coated properly, upon mixing with oil yield greases with superior properties[198].

Mentioned previously was the reported role of fine particle silicas treated with organosilanes in effecting enhanced reinforcement of some elastomers[78, 90, 104]. Patent protection for much of this and similar work is on record[199–201]. Phreaner[202] described the results of extensive studies relating to the influence of silicone oils on silica-filled rubbers of butadiene-acrylonitrile, butadiene-styrene, and chloroprene. Characteristic benefits of the coating were observed, depending on the polymer and curing system. Similar benefits were disclosed[203] for silicone rubbers reinforced with silicone oil-treated silica. Advantages also were demonstrated[204, 205] with the use of silicone oil-treated silica in elastomers containing fluorine. In these applications, too, the influence of the type of curing system was apparent. Benefits with the use of the coated filler were more dramatic using a benzoyl peroxide cure. There is evidence from calcination (800° C) experiments that the reaction of silicone oil with silica is chiefly through the surface silanol groups (see discussion of silica surface structure in Sections IV—E and V—D,-1,-c. Stöber[206] observed that the treatment of amorphous silica with methylchlorosilanes reduced the surface OH concentration from 6.2 micromoles/sq meter to 3.7 micromoles/sq meter. Steric hindrance was held responsible for the less quantitative reaction by the chlorosilane. Exposure to the chlorosilane after calcination permitted the adsorption of only 0.65 micromoles of silane/sq meter.

Esterification of silanol groups on the silica surfaces can be accomplished as a part of the pigment isolation process or performed with the isolated pigment. A number of patents have been issued to members of the duPont group who investigated this process and the performances of the fillers in various elastomers[35, 207]. High tensiles were realized by the use of the estersil in unsaturated polymers, as well as in silicones[89, 208, 209]. Extended aging apparently caused a loss in the organic coating and subsequent large reduction in tensile[89, 209] strength of the silicone vulcanizate. The siloxane rearrangement between filler and polymer was utilized to cure silicone rubber filled with esterified silica with heat alone, in the absence of peroxide[210].

Fine particle silicas also have been treated with isocyanate compounds[211], lactones[212], triazines[212] and organo-metallic complexes[213] to improve their reinforcement of elastomers.

VII. COMPOUNDING AND APPLICATION OF REINFORCING SILICATE AND SILICA FILLERS

In general, the compounding and processing of reinforcing silicate fillers are quite similar to the processes used for other rubber fillers of comparable size, either black or nonblack. As might be expected, however, the increasing use of reinforcing silicas in the past decade has been accompanied by new problems in their application. This is not uncommon in the use of new materials that give desirable and previously unobtainable properties.

For example, in the case of the silicate fillers, the accelerations commonly used in natural rubber are satisfactory with a single important exception. MBT does not give good cures when used alone with calcium silicate[214]. This may result from formation of an inactive calcium salt of the accelerator. When properly activated with a small amount of guanidine, MBT can be used satisfactorily with calcium silicate in natural rubber. MBT alone is satisfactory for SBR compounds loaded with calcium silicate.

The important effect of moisture on rate of cure and physical properties of SBR vulcanizates was observed early in the period when compounding techniques were being developed for this elastomer. These effects were found to be especially pronounced in compounds loaded with Silene EF. Water is not a good compounding ingredient because of volatility which results in variability in the amount of water retained in the stock and also causes porosity in vulcanized compounds. A less volatile polar compound which was found to confer the benefits of water without its disadvantages is diethylene glycol[215, 242]. Later, glycols as a class, were found to have considerable effect on calcium silicate loaded natural rubber compounds as well. The effects of glycol on either natural rubber or SBR loaded with calcium silicate are to speed up rate of cure, and increase modulus, tensile strength, tear resistance and hardness. A good rule of thumb is to use 6 per cent of glycol based on the pigment. Calcium silicate has an unusual effect in neoprene which is worthy of note. In this elastomer it does not affect rate of cure, tensile strength or tear resistance. It increases hardness considerably but most important, from the standpoint of commercial utilization of neoprene, is the fact that hardness of calcium silicate loaded neoprene stock containing glycol does not change during continuous exposure to boiling water[216].

In the case of the reinforcing silicas, the principal problems that have arisen have concerned the type of mixing, stiffness of uncured compounds and acceleration. These problems differ in degree for the anhydrous and hydrated silicas and the answers are different. The latter type, because of low cost, is far more important commercially than the former and for this reason is given greater emphasis in the succeeding text.

The anhydrous silicas, such as Aerosil, have a smaller particle size than the widely used hydrated types or than HAF carbon black. It is recommended[217] that they be used at lower than normal carbon black loadings in order to get processability corresponding to that of black. Hydrated silicas, on the other hand, are generally used at the same volume loading as carbon black when nonblack compounds are desired.

It became obvious early in the commercial use of hydrated reinforcing silica in the United States that some precautions had to be taken when mixing the

filler into natural rubber on an open mill. Early factory trials generally involved small mill batches rather than large Banbury mixes. In some cases, results obtained with factory mixed NR compounds were poorer than laboratory mixes by a considerably greater margin than is normally expected between production and laboratory. These failures to obtain anticipated properties were traced to changes in the compound as a result of mixing on an open mill.

This early silica dispersed readily but, because of its extremely fine particle size, many technologists expected it to be difficult to disperse and resorted to long mixes or to remilling procedures. No harm resulted if this mixing was done

TABLE LII

EFFECT OF TYPE OF MIXING ON PROPERTIES OF SILICA LOADED NR COMPOUNDS

Formula 1

Smoked sheets	100
Zinc oxide	5
Hi-Sil 101	58.5
PBNA	1
Sulfur	3
MBTS	1
TMTDS	0.25
Stearic acid	3

	Mixing conditions				
	Time in Banbury	Temp	Time on mill	Temp	Total mix time
A	10 min	250° F	10 min	210° F	20 min
B	10	250	20	210	30
C	—	—	30	210	30

Formula	Cure at 287° F	300% Modulus	Tensile	Elong.	Duro hard.	Tear lbs/in
1A	7.5 min.	470	1990	610	55	140
	10	1110	3620	615	65	500
	20	1110	3400	610	67	500
	30	1010	3230	605	68	500
	60	880	2960	615	67	450
1B	10	710	2750	610	55	450
	20	980	3160	610	65	500
	30	790	2600	600	65	430
	60	750	2550	620	66	390
1C	7.5	110	510	810	51	70
	10	130	650	755	53	80
	20	600	1740	540	56	100
	30	790	2340	560	61	140
	60	770	2400	565	63	150

in an internal mixer. Mixing on a roll mill or excessive remilling beyond the time needed to incorporate sulfur and accelerators caused loss of properties. This is illustrated in Table LII by results obtained in a direct comparison of silica compounds mixed on a roll mill and in a Banbury[218]. In the Banbury mixes, zinc oxide, sulfur, PBNA and stearic acid were added to the rubber and mixed for two minutes. Half of the silica was added and mixed for four minutes. The rest of the silica was added, mixed for four minutes and the batch dumped after a total of ten minutes. The batch was placed on a roll mill and accelerator masterbatches added and blended. Ten minutes were

required for these operations. In another test, the Banbury batch was milled for 10 minutes before the accelerators were added. This batch had a total of 20 minutes on the roll mill. Conventional practices were followed in milling the batch that was mixed entirely on the open mill. As results in Table LII show, physical properties of the vulcanizate decrease as mixing time on the roll mill increases.

If a roll mill is the only mixing equipment available, the loss of properties shown above can be minimized or prevented in two ways:

1. Mix the complete batch and cut from the mill as quickly as possible. Excessive milling or aging and remilling are unnecessary and undesirable.

2. Mix the rubber and silica only, omitting all softeners, fatty acids, accelerators or other materials, particularly those of a polar nature, that might be adsorbed by the silica. If other fillers such as clay or whiting are being used in the batch, there is no objection to mixing them in at the same time as the silica. After the rubber-filler mixture has been aged for several hours, the final batch can be completed on a roll mill without special precautions and there will be no loss of properties. This procedure[219] differs from masterbatching as the term is commonly understood in that all oils and readily adsorbed materials must be excluded. In ordinary masterbatching the softener is generally added with the filler to improve dispersion.

The reason why the simple masterbatch containing nothing but rubber and silica does not degrade during subsequent mixing is not fully understood. It is possible that when there are no other materials present to be adsorbed by the filler, the rubber penetrates into the filler flocs. Subsequent addition of materials that are more readily adsorbed by the filler does not then interfere with any existing rubber-filler bond. If softener is added to the rubber at about the same time as the silica, it may be adsorbed preferentially and block the rubber away from the filler surface. The prolonged action of a roll mill or, perhaps, the fact that the action is taking place in the open air seems to aggravate this condition more than the faster but less thorough mixing and relative absence of air in a Banbury.

It should be emphasized that the loss of properties described occurs only in connection with open mill mixing and not with an internal mixer. There are no special precautions to be taken if the mixing is done in a Banbury; mixing procedures ordinarily used for black reinforcing fillers can be followed. It should also be emphasized that the loss of properties associated with open mill mixing does not occur when synthetic rubbers are used but only when the elastomer is natural rubber.

Despite their low bulk density, reinforcing silicas mix readily in internal mixers without excessive dusting. Another problem arises where open mills are used because of the tendency of the filler to fly. Where the silica is used together with clay or whiting, the dusting can be minimized by mixing the fillers together and letting the denser material help carry the silica into the rubber. A seemingly obvious solution to this problem is pelletization but this has not yet been put into practice. Carbon black processes, which use small amounts of water, are not applicable to silica. Use of oils or fatty acids to help pelletize the material is not effective because of the silica's great capacity to hold such materials.

Another frequent suggestion is that the silica be put into a latex masterbatch. Good Hi-Sil masterbatches have been made on a sizeable pilot plant scale. These reduce mixing time, eliminate dust, and give improved properties but the favorable factors are overshadowed by problems of economics. Again,

TABLE LIII

EFFECT OF REINFORCING SILICA ON PLASTICITY OF NATURAL RUBBER

Volumes of Hi-Sil 233 per 100 parts of natural rubber*	Mooney plasticity (Large rotor, 4 min at 100° C)
0	25
10	40
15	65
20	105
25	143
30	202

* Smoked sheets given three 10 minute breakdowns on a mill with intervening 30 minute rest periods. All batches were mixed for 12 minutes in a Banbury.

the silica's hydrophilic nature causes difficulties not encountered in making black masterbatches. Slurries of the pigment are by necessity quite dilute and this increases the cost of drying the rubber-filler mixture after it is coagulated.

A. SOFTENERS FOR SILICA LOADED NATURAL RUBBER COMPOUNDS

It was mentioned that the stiffness of uncured compounds is a problem connected with the use of reinforcing silica. This is shown in Table LIII which gives the Mooney plasticities of natural rubber batches containing various loadings of Hi-Sil 233.

Since silica will be most frequently used in white or nonblack colored compounds, the plasticizing effect of softeners which are relatively nondiscoloring

TABLE LIV

PLASTICIZING EFFECT OF VARIOUS SOFTENERS ON NATURAL RUBBER LOADED WITH 25 VOLUMES OF REINFORCING SILICA

	Mooney plasticity (ML 4 at 100° C)			Williams plasticity (3 min at 100° C)		
	Parts of softener per 100 parts rubber					
Softener	3	5	10	3	5	10
Fortex		70	45		325	265
Liquid Plastone		65	37		340	280
Liqro		78	53		340	265
Rosin oil		85	49		350	265
Stearic acid	108	86		405	360	
Lauric acid	109	85		410	360	
Oleic acid	110	90		410	355	
Cottonseed fatty acid	115	88		415	355	
HSC 13		86	49		365	300
Wool grease		85	51		370	285
Palm oil	114	100		435	400	
RPA #3*		102	89		435	400
Pepton 22*		101	92		460	430
Cumar P-10		108	85		415	370
Sundex 53		110	88		425	380
Circosol 2XH		109	95		455	390
Petrolatum		112	90		460	395
Forum 40		112	94		460	420
Dipolymer oil		114	96		445	430
Circo Light		114	95		460	440
Bondogen		128	118		465	435
No softener		138			480	

* 0.5 and 1 part used instead of 5 and 10. These mixes were made at 107° to 116° C.

is of more interest than that of dark colored or staining softeners, resins, tars or pitches. Table LIV shows Mooney plasticities produced by a representative group of such softeners on natural rubber containing 25 volumes of Hi-Sil 233[220]. Several fatty acids were included to see if there would be any choice among them as far as softening power is concerned. All seemed to be about equally effective. It is interesting to note that the best softeners are those of vegetable origin. Fortex is a chemically treated vegetable acid; Liqro is tall oil; Plastone is based on rosin oil; rosin oil itself is very effective. Lanolin also is a good softener for silica compounds. The chemical plasticizers are less effective although better than petroleum based materials which appear to be of little value.

B. ACCELERATION

In 1948 when reinforcing silica first became commercially available there was no information in the literature nor accumulation of experience in the hands of compounders that would help them in dealing with this new, different material. Long vulcanization times were required to "cure" compounds loaded with reinforcing silica and accelerated with normal amounts of accelerator. For example, a compound with 30 volumes loading might require two hours to vulcanize with a single accelerator such as 1.5 parts of a guanidine, one part of an aldehyde-amine or thiazole or 0.5 part of a thiuram or dithiocarbamate. Obviously, the first major problem in connection with the use of fine particle silica as a rubber filler was to obtain a reasonable rate of cure.

Reinforcing silicas whether hydrated or anhydrous tend to adsorb accelerators. Therefore, in formulating silica loaded compounds it is necessary to use more than the ordinary amount of accelerator and also to use certain activators. Reduction of vulcanization time was achieved with combinations of primary and secondary accelerators in greater than normal amounts. It was accomplished first in NR by using 1 phr of a thiazole and 0.25 phr of a thiuram, a combination that would be regarded as extremely "scorchy" for ordinary NR compounds. It was also found advisable to use additives such as glycols or amines if fast "tight" cures were desired. These will be dealt with later in more detail.

Information about thiazole-thiuram accelerator combinations was first published[221, 222] in 1949 and comparisons of physical properties and scorch times imparted by different thiazoles with several thiurams in NR and SBR were given. MBT, Ethylac and Cuprax imparted somewhat better physical properties than other thiazoles in NR but were also more scorchy. MBTS combinations did not impart the highest properties but they had long scorch times and proved, in production, to be a useful compromise. Results obtained by using MBTS-TMTDS combinations to vulcanize NR and GR-S loaded with an early Hi-Sil are shown in Tables LV and LVI.

Although thiazole-thiuram combinations were used in early commercial production of silica loaded rubber goods, they were never regarded as too satisfactory because of their tendency to scorch and to revert with overcure. Later work was done with combinations of thiazoles and guanidines, an accelerator mixture that had frequently proven useful in the historical past for vulcanizing slow curing elastomers. It was found[223] that more satisfactory cures were obtained with thiazole-guanidine combinations. Such combinations need an additional activator somewhat more than do the thiazole-thiurams. In the United States liquid glycols, such as diethylene glycol[243], are used to some extent although less volatile solid polyglycols are generally preferred. Amine activators give even faster cures. Triethanolamine is commonly used in the United

TABLE LV

VARIOUS LOADINGS OF REINFORCING SILICA IN THIAZOLE–THIURAM ACCELERATED NR

Formula 2

Smoked sheets	100
Hi-Sil 101	As shown
Zinc oxide	5
PBNA	1
MBTS	1
TMTDS	0.25
Sulfur	3
Stearic acid	3

Loading	Williams plasticity	Mooney scorch, minutes	Min. cured at 287° F	300% Modulus	Tensile	Elongation	Durometer hardness	Tear lbs/in
10 vols (19.5 parts)	.185	35	12	400	3625	665	42	480
			15	675	4700	640	55	410
			20	775	4200	590	58	270
			30	725	3450	555	58	220
20 vols (39 parts)	.300	27	12	250	1825	610	45	220
			15	875	3850	600	59	420
			20	875	3650	590	60	290
			30	775	3475	610	59	330
30 vols (58.5 parts)	.340	21	7.5	675	2250	575	55	290
			10	1200	3725	585	65	560
			15	1250	3450	575	67	540
			20	1100	3200	585	66	510
			30	1050	3000	585	66	500

Loading	Min cured at 260° F	Rebound, % (Goodyear-Healy)	Temp rise, ° F (Goodrich Flexometer)
10 vols	65	80	8
	80	81	9
	115	83	9
20 vols	65	80	17
	80	75	18
	115	78	23
30 vols	65	69	38
	80	69	38
	115	68	44

Loading	Min cured at 287° F	Compression set, % (method B)	DeMattia flexing (In/90,000 flexes)
10 vols	15	34	.08
	20	19	.16
	30	14	.19
20 vols	15	30	.08
	20	24	.11
	30	18	.12
30 vols	15	38	.05
	20	31	.04
	30	20	.11

TABLE LVI

30 VOLUMES OF REINFORCING SILICA IN THIAZOLE–THIURAM ACCELERATED GR–S

Formula 3	
GR-S 1000	100
Hi-Sil 101	58.5
Zinc oxide	5
PBNA	1
MBTS	1.2
TMTDS	0.15
Sulfur	3
Coumarone (100° C m.p.)	15
Diethylene glycol	3.5

Cure at 280° F, min	300% Modulus	Tensile psi	% Elongation	Durometer hardness 30 sec	Tear lbs/in	Scorch time min
10	470	2510	715	55	270	18.5
15	670	2550	620	60	270	
30	720	2470	585	60	260	
45	620	2480	605	58	240	
60	570	2230	590	56	190	
90	570	2240	595	56	180	

States or hexamine if transparent stocks are desired. In Europe, some of the widely used activators contain such materials as hexane triol, dicyclohexylamine and mixtures of fatty acid salts of dicyclohexylamine with diethylene glycol and formamide.

This use of a glycol or amine additive was found to give a control over curing time that permitted a range from slow cures to cures even faster than were obtainable with thiazole-thiurams. In addition to making possible less scorchy

TABLE LVII

VULCANIZATION OF 30 VOLUME HI–SIL 233 NR COMPOUNDS WITH THIAZOLE–THIURAM AND THIAZOLE–GUANIDINE COMBINATIONS

Formula	4	5
Smoked sheets	100	100
Zinc oxide	5	5
Hi-Sil 233	58.5	58.5
Antiox. 2246	1	1
Sulfur	3	3
MBTS	1	0.8
TMTDS	0.5	—
DOTG	—	1.2
Triethanolamine	2	1
Stearic acid	3	3

Formula	Cure at 287° F, min	300% Modulus	Tensile	Elongation	Durometer hardness	Tear lbs/in
4	10	1180	3740	590	70	810
	15	1210	3750	590	71	740
	30	1190	3520	580	74	740
	45	1140	3450	580	76	750
	60	1110	3320	580	78	680
5	7.5	670	3520	680	53	640
	15	870	3820	660	58	750
	30	1030	3830	640	62	770
	45	1040	3790	610	62	720
	60	1080	3760	600	65	680

TABLE LVIII

COMPARISON OF EFFECT OF COMMON ACTIVATORS IN SILICA LOADED NATURAL RUBBER

Formula	6	7	8	9	10	11
#1 Smoked sheets	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Hi-Sil 233	58.5	58.5	58.5	58.5	58.5	58.5
Agerite White	1	1	1	1	1	1
MBTS	0.8	0.8	0.8	0.8	0.8	0.8
DPG	1.2	1.2	1.2	1.2	1.2	1.2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5
TEA	1	—	—	—	—	—
Hexamine	—	1	—	—	—	—
Diethylene glycol	—	—	1	—	2	—
Carbowax 4000	—	—	—	1	—	2
Stearic acid	3	3	3	3	3	3
Mooney scorch (mins to 5 pt rise above min visc. S.R. 250° F)	12.25	21.5	16	20.5	9	13.5

For-mula	Cure at 287° F	300% mod.		Tensile		Elong.		Duro. hard			Hysteresis
		Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged	Tear	ΔT
6	7.5	510		3550		720		63		710	
	15	750		3740		660		69		770	
	30	820	1570	3670	3360	640	520	76	82	760	
	45	870	1630	3600	3270	620	500	76	82	700	
	60	840	1620	3600	3180	640	500	77	83	640	67
7	7.5	260		3050		780		53		350	
	15	560		3600		680		62		710	
	30	750	1290	3600	3460	650	560	71	75	740	
	45	830	1430	3570	3390	610	550	73	77	750	
	60	860	1430	3600	3180	600	520	76	80	740	76
8	7.5	300		2410		690		50		320	
	15	540		3260		680		59		630	
	30	770	1560	3560	3240	630	510	68	79	730	
	45	790	1530	3580	3350	630	530	70	83	690	
	60	820	1630	3490	3170	610	500	72	83	670	95
9	7.5	250		2630		800		56		190	
	15	520		3270		670		63		600	
	30	630	1180	3460	3590	660	640	72	75	680	
	45	700	1320	3520	3440	650	580	72	77	670	
	60	700	1290	3500	3420	650	600	72	78	690	73
10	7.5	580		3530		670		63		740	
	15	780		3730		650		68		750	
	30	830	1840	3650	3510	620	500	73	84	710	
	45	830	1770	3550	3160	610	480	74	84	700	
	60	830	1740	3460	2870	610	440	75	86	630	71
11	7.5	430		3440		710		62		610	
	15	680		3840		680		67		740	
	30	750	1330	3680	3660	640	580	69	75	660	
	45	760	1240	3670	3370	640	560	72	78	720	
	60	770	1240	3800	3420	660	580	76	78	630	73

stocks, the thiazole-guanidine combinations also resulted in compounds with much less tendency to overcure. This is shown by the results in Table LVII which compare 30 volumes of Hi-Sil 233 in NR using these two types of accelerator combinations[220].

Thiazole-guanidine combinations have continued to be the most widely used acceleration for silica loaded compounds ever since they were first reported.

A comparison between DPG, DOTG and TPG as secondary acclerator in this combination was made during early work with Hi-Sil 101. The first two were found equal in respect to activity, scorch and aging while TPG was much less active.

c. ACTIVATORS

A comparison of the effect of activators commonly used in silica loaded compounds in the United States is shown in Table LVIII. The two glycols, it will be noted, have a greater margin of processing safety than a compound activated with an equal amount of triethanolamine but also have slightly poorer physical properties. Increasing the glycol increases scorch and also improves physicals. The effect of increasing the triethanolamine is shown in Table LIX. This plainly shows the very marked effect of TEA on rate of cure and on physical properties particularly modulus and hardness.

TABLE LIX

EFFECT OF INCREASED TEA IN SILICA LOADED NR

Formula	12	13	14	15
#1-RSS	100	100	100	100
Hi-Sil 233	58.5	58.5	58.5	58.5
ZnO	5	5	5	5
PBNA	1	1	1	1
MBTS	0.8	0.8	0.8	0.8
DOTG	1.2	1.2	1.2	1.2
TEA	0.5	1	2	3
Sulfur	3	3	3	3
Stearic acid	3	3	3	3

For-mula	Cure at 287° F	300% modulus		Tensile		Elong.		Hard.		Tear
		Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged	
12	7.5	170		1440		690		40		130
	15	490		2950		690		49		530
	30	730		3220		640		53		740
	45	750	1340	3480	3690	650	580	58	66	610
	60	810	1320	3360	3730	630	590	59	70	680
13	7.5	670		3520		680		53		640
	15	870		3820		660		58		750
	30	1030	1620	3830	4130	640	600	62	70	770
	45	1040	1660	3790	4010	610	600	62	69	720
	60	1080	1760	3760	3880	600	560	65	71	680
14	5	880		3890		670		55		800
	7.5	1100		4020		650		62		870
	10	1140		3900		620		63		790
	15	1340	1900	4080	4200	610	580	65	73	730
	30	1500	2100	3870	4030	570	540	70	75	710
	45	1430	2060	3800	3870	560	530	69	76	640
15	5	920		4060		670		65		790
	7.5	1220	2070	3940	4190	600	560	70	82	800
	10	1230	2170	3740	3980	580	530	72	83	710
	15	1420	—	3880	—	560	—	75	—	720
	30	1460	2240	3680	3600	540	480	80	89	680
	45	1500		3530		520		78		560

Aging for Tables LVIII and LIX: 14 days in air oven at 158° F.

Tests of many other activators have not been reported previously because they have been less satisfactory than the commoner materials in some respect.

For example, dipropylene glycol, polypropylene glycol and hexylene glycol were tested for activating ability and showed no advantage over diethylene glycol. Thiodiglycol proved inferior. Trigamine, a mixture of mono-, di-, and triethanolamines, has proven less effective than triethanolamine. Pyridine is more effective but is not a desirable material to use because of its toxicity.

Use of dicyclohexylamine has been advocated in Germany as an activator for compounds loaded with reinforcing silica[224]. This material was tested against equal weights of DEG and TEA in both NR and SBR. It was not any more effective and since it is more expensive it would be inferior as an activator on an equal cost basis.

Although liquid glycols are more difficult to handle than solid polyglycols and are also more volatile, they may be more suitable for use in white and delicate pastel colored compounds.

The high molecular weight, solid glycols all undergo a certain amount of darkening when heated with hydrated silica, calcium silicate, sodium silico aluminate or hard clay. This can be demonstrated by heating a mixture of two parts of the glycol with one part of filler in an oven for two hours at 310° F. Mixtures made with diethylene glycol or with Polyethylene Glycol 200, which is a low m.w. liquid, do not discolor. Mixtures made with solid polyglycols such as the Carbowaxes or D-C Polyglycols all turn dark. Discoloration may result from some catalyst or other additive used in polymerization of the glycol. Metal ion content of the filler also has some bearing on discoloration. A silica having low content of extraneous ions (Hi-Sil X303) causes less discoloration of a high m.w. polyglycol than does Hi-Sil 233 which is, in turn, distinctly better than Hi-Sil 101. A calcium silicate, a sodium silico aluminate and a rubber grade clay all caused more discoloration than any of the silicas.

It should be noted that the test described here is an exaggerated one designed purposely to give maximum discoloration. The ratio of glycol to filler is unrealistic as far as practical compounding is concerned and the heating period is excessive. It is doubtful that discoloration will be noted in normally colored stocks but it will be observable in white and, to a lesser extent, in transparent compounds.

The discovery that diethylene glycol was an effective inhibitor of sunlight discoloration of white NR compounds was an unexpected incidental result of the early work on its use as a cure activator[225]. This effect was first noticed when glycol was added to an air cured Hi-Sil loaded sheeting stock to increase the rate of cure. The resulting vulcanizate was much whiter than a glycol-free control after sunlight exposure. Later, it was found that glycol caused the same improvement in zinc oxide loaded stocks that contained no silica.

D. USE OF ZINC OXIDE AND FATTY ACID

Almost every rubber compound written since an 1849 patent[226] was granted for combinations of rubber, sulfur and zinc compounds has contained at least 3 phr of zinc oxide. It has been generally believed that this entered into the vulcanization mechanism by reacting with fatty acid to form zinc soaps which in turn reacted with the accelerator.

Considering the results[181] both of early work on Hi-Sils 101 and 202 and of later work on Hi-Sil 233, it seems impossible to generalize about the use of zinc oxide and stearic acid with silica fillers. Instead, it appears that this may have to be determined for each system of acceleration.

Table LX

Effect of Silica in Simple Unextracted NR–Sulfur Mix Containing Silica

Formula	16	17	18	19
Smoked sheets	100	100	100	100
Zinc oxide	—	5	—	5
Hi-Sil 101	—	—	58.5	58.5
Sulfur	8	8	8	8

Formula	ZnO	Mins cure at 287° F	300% modulus	Tensile	Elong.	Hard.	Tear
16	0	120	40	740	980	32	50
		240	90	1420	930	35	100
		360	130	2010	850	38	130
17	5	120	90	1350	830	32	90
		240	140	1940	800	37	120
		360	200	2500	760	41	140
18	0	120	1500	3220	550	75	430
		240	1890	3150	490	80	520
		360	2200	2850	410	85	380
19	5	120	1630	3010	480	75	230
		240	1860	2960	480	81	510
		360	2000	2670	450	86	310

Table LXI

Influence of ZnO and Stearic Acid on Silica Loaded NR Compound Accelerated with Thiazole–Thiuram

Formula	20	21	22	23
#1 Smoked sheets	100	100	100	100
Zinc oxide	5	5	—	—
Hi-Sil 202	58.5	58.5	58.5	58.5
MBTS	1	1	1	1
TMTDS	0.2	0.2	0.2	0.2
Sulfur	3	3	3	3
PBNA	1	1	1	1
Stearic acid	3	—	—	3

Formula	Parts ZnO & stearic	Mins Cure 287° F	300% modulus	Tensile	Elong.	Hard.	Tear
20	ZnO 5	15	450	2340	670	57	140
	Stearic 3 acid	30	510	2450	660	63	150
		45	500	2330	660	67	170
		60	610	2520	660	68	210
		90	680	2670	650	69	170
21	ZnO 5	15	810	2160	570	73	110
	Stearic 0 acid	30	880	2310	570	72	100
		45	870	2230	550	73	120
		60	880	2580	600	72	130
		90	940	2170	530	72	160
22	ZnO 0	15	380	1820	710	66	140
	Stearic 0 acid	30	480	1830	640	67	150
		45	510	1940	640	68	190
		60	620	2270	650	70	220
		90	720	2350	640	71	380
23	ZnO 0	60	300	1830	750	48	140
	Stearic 3 acid	90	360	2000	750	52	190

The use of zinc oxide is desirable in a simple unextracted NR-sulfur mix without accelerators. When a reinforcing silica is present, however, zinc oxide is not necessary. This fact is illustrated by the results in Table LX. Results of similar tests in SBR were meaningless because of the very poor physical properties of SBR-sulfur mixtures.

Thiazole-thiuram accelerated compounds.—Silica loaded NR compounds accelerated with a thiazole-thiuram mixture have about equal properties if both

TABLE LXII

INFLUENCE OF ZnO AND STEARIC ACID ON SILICA LOADED NR COMPOUND ACCELERATED WITH THIAZOLE-GUANIDINE

Formula	24	25	26	27
Smoked sheets	100	100	100	100
Zinc oxide	5	5	—	—
Hi-Sil 233	58.5	58.5	58.5	58.5
MBTS	0.8	0.8	0.8	0.8
DPG	1.2	1.2	1.2	1.2
Sulfur	3	3	3	3
Triethanolamine	1	1	1	1
Stearic acid	—	3	—	3

Compound	Parts ZnO & stearic	Cure at 287° F	300% mod.	Tensile	Elong.	Duro. hard.	Tear lbs/in
24	ZnO 5	7.5	980	3210	580	75	230
	Stearic 0	15	1250	3500	560	79	270
	acid	30	1390	3580	540	83	650
		45	1330	3650	570	84	740
		60	1410	3540	550	86	670
		120	1270	3290	550	87	700
25	ZnO 5	7.5	420	2580	700	56	190
	Stearic 3	15	570	2960	650	65	370
	acid	30	820	3260	620	71	580
		45	880	3250	590	73	670
		60	950	3320	580	76	630
		120	1020	3250	570	82	710
26	ZnO 0	7.5	600	2960	690	76	200
	Stearic 0	15	700	3210	700	73	270
	acid	30	630	3290	740	78	380
		45	560	3220	770	78	400
		60	560	3140	770	78	470
		120	520	3110	800	80	380
27	ZnO 0	7.5	330	2130	750	68	190
	Stearic 3	15	390	2480	770	72	210
	acid	30	390	2690	830	73	250
		45	370	2540	820	76	320
		60	360	2660	870	78	340
		120	330	2480	880	82	340

zinc oxide and fatty acid are present or if zinc oxide is present in the absence of fatty acid[181]. Use of fatty acid without zinc oxide slows the cure badly. These points are illustrated in Table LXI.

Increasing the ZnO to 15 phr in Formula 21 increased hardness and modulus considerably but had no other effect. Increasing the ZnO to 15 phr in Formula 20 reduced tensile very slightly.

Substitution of MgO for ZnO in either Formula 20 or 21 gave lower modulus

and tensile strength. Tear of the MgO stocks was slightly higher, possibly because of a less tight cure.

Thiazole-guanidine accelerated compounds.—When a guanidine replaces the thiuram as secondary accelerator in an NR compound loaded with precipitated reinforcing silica, it is no longer necessary to use both zinc oxide and stearic acid to get the best properties. Instead, better ultimate properties are obtained with zinc oxide present but stearic acid absent. Since natural rubber contains

TABLE LXIII

INFLUENCE OF ZnO AND STEARIC ACID ON SILICA LOADED NR COMPOUNDS USING ZINC SALT ACCELERATORS

Formula	28	29	30	31
Smoked sheets	100	100	100	100
Zinc oxide	4.75	4.75	—	—
Hi-Sil 202	58.5	58.5	58.5	58.5
Zenite*	1.33	1.33	1.33	1.33
Methyl Zimate**	0.25	0.25	0.25	0.25
Sulfur	3	3	3	3
PBNA	1	1	1	1
Stearic acid	3	—	—	3

For-mula	Parts ZnO & stearic	Mins cure 287° F	300% modulus	Tensile	Elong.	Hard.	Tear
28	ZnO 4.75	15	540	2550	680	62	170
	Stearic 3	30	530	2340	670	63	180
		48	580	2500	680	71	160
		60	550	2510	670	71	200
		90	600	2520	660	72	180
29	ZnO 4.75	15	850	1890	520	78	120
	Stearic 0	30	890	2280	550	78	130
	acid	45	910	2510	600	81	130
		60	870	2650	610	80	130
		90	820	2680	630	82	130
30	ZnO 0	15	430	1430	640	62	110
	Stearic 0	30	470	1900	670	68	160
	acid	45	530	2040	670	71	160
		60	570	2040	670	71	260
		90	540	2260	680	71	220
31	ZnO 0	15	110	850	770	48	90
	Stearic 3	30	180	1350	800	54	120
	acid	45	230	1480	770	54	130
		60	240	1730	810	51	150
		90	240	1760	780	57	160

* Zinc benzothiazolyl sulfide.
** Zinc dimethyl dithiocarbamate.

some natural fatty acid and guanidine acceleration needs very little, if any, it appears that large amounts of added fatty acid, if not needed to aid processing, are deleterious because they reduce the rate and state of cure. It is interesting to note that thiazole-guanidine accelerated silica compounds containing neither zinc oxide nor stearic acid are better than those containing the fatty acid only. These results[181] are shown in Table LXII.

These relationships do not necessarily hold if metallic oxides other than zinc oxide are used or if zinc oxide is used in combination with another oxide. In the case of zinc oxide-litharge mixtures, a relatively high stearic acid content

gave faster cures than a low one[181]. Magnesium oxide also acted somewhat differently than zinc oxide in this type of compound. There was little difference in rate of cure or physical properties between a stock containing magnesium oxide only and one containing both magnesium oxide and stearic acid except that the latter had lower modulus and hardness as would be expected. Both of the magnesium oxide compounds were somewhat faster curing than their zinc oxide counterparts but had lower moduli, hardness and tear resistance and about equal tensile strength.

Zinc salt acceleration.—Silica loaded NR compounds accelerated with zinc salt accelerators such as zinc benzothiazolyl sulfide (Zenite) and zinc dimethyl

TABLE LXIV

SILICA LOADED NR COMPOUNDS ACTIVATED WITH LITHARGE

Formula	32	33	34
Smoked sheets	100	100	100
Hi-Sil 202	58.5	58.5	58.5
Litharge	13.7	13.7	12.5
MBTS	1	1	1
Ledate*	0.37	0.37	0.37
Sulfur	3	3	3
PBNA	1	1	1
Stearic acid	—	3	—
Lead stearate	—	—	4.05

Formula	Cure at 287° F, min	300% modulus	Tensile	Elongation	Duro. hard.	Tear lbs/in
32	15	1790	4130	560	73	830
	30	1860	3930	520	77	660
	45	2010	3770	500	78	720
	60	1870	3530	500	79	700
	90	1730	3560	530	77	690
33	15	1400	3720	570	68	640
	30	1720	3770	530	71	650
	45	1820	3390	490	72	580
	60	1660	3320	490	72	580
	90	1630	3210	480	72	530
34	15	1500	3960	590	70	560
	30	1770	3690	510	75	600
	45	1870	3630	500	80	440
	60	1820	3350	480	81	480
	90	1760	3160	470	80	540

* Lead dimethyl dithiocarbamate.

dithiocarbamate (Methyl Zimate) cure more quickly and have better properties if both zinc oxide and stearic acid are also present. In this case, added zinc oxide alone does not appear helpful[181]. Stearic acid alone retarded cure badly. This is shown in Table LXIII. Along this same line, substitution of zinc stearate for zinc oxide and stearic acid in silica loaded NR accelerated with either thiazole-thiuram combinations or with zinc salts did not give satisfactory results.

Replacement of ZnO with litharge.—Silica loaded NR compounds cure faster and have better properties if litharge is used as an activator in place of zinc oxide[227]. This can be seen by comparing the results for Compound 32 in Table

LXIV with Compound 20 in Table LXI. Neither stearic acid nor lead stearate appears to be desirable with litharge activated compounds. As mentioned earlier this does not hold true for mixtures of zinc oxide and litharge where stearic acid definitely increases rate of cure but does not have much effect on other properties. This is shown in Table LXV.

Fatty acids.—Much of the early work with the hydrated reinforcing silicas was done in the 1940's when the natural rubber that was available was of poor and uneven quality. In some cases it was found that one part of fatty acid was not enough because the rubber was deficient in natural fatty acid and was "starved" by the adsorptive pigment. This sometimes caused low tensile and tear strengths and use of at least three parts of fatty acid was recommended at that time for compounds containing high loadings of reinforcing silica. Since poor quality rubber has ceased to be a problem and since excess fatty acid is ob-

TABLE LXV

EFFECT OF INCREASED STEARIC ACID ON RATE OF CURE OF ZnO–LITHARGE ACTIVATED COMPOUNDS

Formula	35	36
Smoked sheets	100	100
Zinc oxide	5	5
Litharge	3	3
Hi-Sil 101	57	57
Santocure	1	1
DPG	0.5	0.5
Sulfur	3.5	3.5
PBNA	1	1
Stearic acid	1	3

Formula	Cure at 287° F min	300% modulus	Tensile	Elong.	Hard.	Tear
35	10	765	3060	630	68	480
	15	910	3290	600	70	580
	30	1180	3560	575	74	540
	60	1230	3330	550	76	480
36	10	820	3400	620	68	550
	15	1010	3530	615	73	570
	30	1110	3080	580	76	460
	60	1080	2860	560	79	450

viously undesirable in many cases, it is suggested that fatty acid content be held to the low side of a one to three phr range unless more is needed for processing reasons. For example, fatty acid need not be added for activation of SBR but it is useful in preventing sticking of any mineral filled LTP compound.

Comparisons between stearic acid, oleic acid, lauric acid, palmitic acid and cotton seed fatty acid indicated that there was little choice between them in regard to activation or physical properties of the unaged or aged vulcanizate. Differences in plasticizing ability are not great as can be seen by reference to Table LIV.

Replacement of stearic acid by lanolin in silica loaded compounds has been suggested in Germany. When this was done using a recipe similar to Compound 25 in Table LXII, the compound containing lanolin was slow curing and had poorer modulus, tensile strength and tear resistance than the one containing stearic acid. Any advantage in use of lanolin was not apparent in this test.

E. ANTIOXIDANTS

Any of the nonstaining antioxidants are satisfactory with reinforcing silica except where a dead white is desired. In the latter case, more care must be exercised because reactions occur between reinforcing silicas and certain antioxidants, producing tints that are very faint but noticeable in dead whites[228]. This can be shown by grinding together one part of antioxidant and fifty parts of silica and heating the mixture for 15 minutes at 150° C. Such American antioxidants as Agerite Gel, Agerite Stalite, Flectol H, Deenax, Ionol, Santowhite Powder, Wingstay S, 425, and 2246 give no color reaction with silica in this test. On the other hand, Agerites White and Alba, Aminox, and Stabilite Alba produce faint coloration. It is emphasized that in these cases, the tints are too faint to be noticed in anything except a dead white compound. Silica compounds containing any of the antioxidants mentioned have excellent retention of properties and good resistance to the deteriorating effects of aging.

F. SILICA IN SBR AND NBR TYPE RUBBERS

As with natural rubber, the use of reinforcing silica in styrene/butadiene rubber (SBR) or in nitrile/butadiene rubber (NRB) results in properties that are closer to those imparted by carbon black than can be obtained with any other nonblack filler available at present.

This reinforcement is of far greater relative importance in SBR and NBR than it is in natural rubber. Natural rubber, and other elastomers which crystallize when stretched, will still have fairly good physical properties even when loaded with the cheapest fillers. This is not true in the case of SBR, NBR, or similar elastomers that remain amorphous under all conditions including stretching. Better quality fillers are much more essential in the manufacture of rubber goods from these rubbers than from natural rubber. If good properties are required in anything other than a black stock, cheap clays or whitings cannot be used. Use of reinforcing silica is essential.

Several points should be particularly kept in mind in compounding SBR with reinforcing silica. The first of these, as with natural rubber, is that more acceleration is needed than with other fillers. Thiazole-thiuram combinations are more satisfactory than they are in natural rubber because there is much less tendency for reversion with overcure. Combinations of 1.0 to 1.25 parts of MBTS with 0.25 to 0.15 parts of TMTDS are very good. Combinations of 0.75 to 1.25 parts of MBTS with 1.75 to 1.25 parts of DOTG also give excellent cures. It must be remembered that either combination will also need about three parts of a glycol or one or more parts of triethanolamine to give a fast cure[243].

As is true when other nonblack fillers are used in SBR, addition of a coumarone-indene resin helps bring out the best tensile and tear properties. About ten parts of resin should be used in compounds containing 30 volume loadings of silica and proportionately smaller amounts for lower loadings. Additional fatty acid is not needed with silica in the older, hot polymerized types of SBR. Two or three parts of stearic acid may be needed when low temperature polymerized rubber (LTP) is used because silica tends to make such compounds sticky.

In using either type of SBR, it is not necessary to observe any special precautions in mixing silica stocks. Excessive mixing on an open mill does not lead to loss of physical properties as it does in the case of natural rubber. There-

fore, it is not necessary to take silica loaded SBR batches off the mill quickly, nor is it necessary to mix filler/elastomer masterbatches as was suggested for natural rubber.

The excellent physical properties imparted to both types of SBR and to NBR by reinforcing silica are shown in Table LXVI[229].

TABLE LXVI

PHYSICAL PROPERTIES IMPARTED TO SBR AND NBR COPOLYMERS BY REINFORCING SILICA

Formula	37	38		39
SBR 1000	100	—	NBR (Hycar 1041)	100
SBR 1502	—	100	Zinc oxide	5
Zinc oxide	5	5	Hi-Sil 233	58.5
Hi-Sil 233	58.5	58.5	Antiox. 2246	2
Antiox. 2246	1	2	MBTS	0.75
MBTS	1.2	1.25	DPG	1.5
TMTDS	0.15	—	Sulfur	1.5
DOTG	—	1.75	Dioctyl phthalate	10
Sulfur	3	3	KP-140	10
Diethylene glycol	3.5	—	Stearic acid	1.5
Triethanolamine	—	1		
Coumarone (100° C m.p.)	15	10		
Stearic acid	—	3		

Formula	Cure min	300% modulus	Tensile lbs/sq in	Elongation	Duro. A hardness	Crescent tear lbs/in
37	15 at 280° F.	380	3030	830	64	340
	20	445	3250	765	65	320
	30	460	3230	720	66	285
	45	495	3140	680	67	270
	60	495	3120	675	69	265
	90	525	3130	655	67	260
38	15 at 287° F.	810	3440	620	63	260
	30	1040	3850	590	68	310
	45	1150	4140	590	68	320
	60	1160	3900	560	70	290
	90	1140	3710	560	71	300
39	10 at 310° F.	310	3200	820	65	350
	20	400	3270	740	69	360
	30	460	3560	720	69	350
	45	510	3420	660	70	330
	60	540	3520	650	70	330

G. SILICA IN CHLOROPRENE RUBBER

Reinforcing silica is an excellent loading material for neoprene. Organic acceleration is not often used with this polymer and the adsorptive nature of the silica filler does not need to be considered in developing a suitable compound. No unusual techniques are needed either in mixing or in curing silica loaded neoprene stocks.

Silicas impart much higher tensile and tear strength to neoprene than can be obtained with other nonblack fillers and have less effect on elongation. When a high loading, such as 40 volumes, is used, silica gives the same hardness and much better tear resistance than easy processing channel black although its tensile strength is slightly lower. At this loading, the elongation of the black stock is barely half that of the silica compound. Use of a small amount of Per-

malux (DOTG salt of dicatechol borate) is usually desirable in silica loaded neoprene to speed up the rate of cure.

It has been reported[230,231] that use of glycol or amine activators was not desirable with chloroprene polymers because they retard cure and reduce physical properties other than hardness which is increased.

The properties imparted by 20 volumes of reinforcing silica to Neoprene GN are shown in Table LXVII[229].

H. SILICA IN BUTYL RUBBER

Use of reinforcing silica is the best method of producing satisfactory nonblack compounds from butyl rubber. No really practical nonblack butyl compounds suitable for factory production were ever made before reinforcing silica became readily available. Clay, whitings, and diatomaceous earth were used to some extent but never gave satisfactory tensile nor tear strength. Some of the silicates gave better properties but were difficult to disperse. Use of hydrated silica resulted in easily processable stocks with better properties than those obtained from the semireinforcing blacks commonly used in butyl since it became available in 1939.

TABLE LXVII

PHYSICAL PROPERTIES IMPARTED TO NEOPRENE BY REINFORCING SILICA

Formula 40

Neoprene GN	100
Magnesium oxide	4
Zinc oxide	5
Hi-Sil 233	39
Permalux	1
PBNA	1
Process oil	10

Cure at 287° F min	300% modulus	Tensile lbs/sq in	Elongation	Duro. A hardness	Crescent tear lbs/in
10	390	1950	1000	51	310
15	700	3170	980	57	500
30	1010	3620	850	60	520
45	1140	3630	780	62	460
60	1230	3590	740	63	430

Hydrated silica is readily mixed into butyl and disperses without difficulty. A silica-filled butyl compound will stick to mill and calender rolls but this sticking can be prevented entirely by use of one or two parts of an ester such as tributoxyethyl phosphate or butoxyethyl diglycol carbonate[232].

Excellent cures of silica loaded butyl can be obtained by use of two parts of TMTDS or by a combination of one part of Tellurac with one part of Zenite[232]. The former is recommended for white or pastel compounds, because Tellurac produces a yellowish discoloration which is not noticeable in reds, yellows or greens but is readily discernible in whites, greys, blues or pastels. Diethylene glycol increases the rate of cure in either case.

Black butyl compounds have generally been vulcanized with two parts of elemental sulfur. Theoretically, only a fraction of this amount is needed because of the high degree of saturation of butyl rubber, but in practice good vulcanizates are not obtained with elemental sulfur unless at least 1.5 to 2 phr are used. Since this amount of sulfur is in excess of that which reacts with the

TABLE LXVIII

PHYSICAL PROPERTIES IMPARTED TO BUTYL RUBBER BY REINFORCING SILICA

Formula 41

Butyl 265	100
Zinc oxide	5
Hi-Sil 233	39
Sulfur	1
Sulfasan R	1.5
TMTDS	2
Diethylene glycol	2
Paraffin	0.75
Tributoxy ethyl phosphate	1

Cure at 307° F, min	500% Modulus	Tensile lbs/sq in	Elongation	Duro. A hardness	Crescent tear lb/in
7.5	280	2160	1020	55	300
10	370	2410	960	57	350
15	480	2540	910	56	280
20	520	2540	880	58	300
30	600	2600	840	62	290
60	690	2590	800	63	300

double bonds in the polymer, the excess appears as an unsightly gray bloom. This bloom is objectionable on the surface of otherwise brightly colored butyl rubber goods. Well cured compounds which do not bloom can be obtained by using a combination of elemental sulfur with an organic sulfide[233]. The amount of elemental sulfur is less than that which will bloom but is not sufficient for a good cure. Additional sulfur in nonblooming form is provided by use of a material such as Sulfasan R (4,4′-dithiodimorpholine)[234]. Typical physical properties imparted to silica loaded butyl by this type of curing system are shown in Table LXVIII[229].

Heat treatment of butyl rubber compounds loaded with reinforcing silica results, as it also does in the case of carbon black, in enhancement of the physical properties of the vulcanizate[108]. In the case of silica, however, it is necessary to use certain chemical promoters to bring about thermal interaction between the filler and polymer. These are not necessary in heat treating black-loaded butyl. Materials which were first found to be effective promoters are p-quinone dioxime, p-quinone dioxime dibenzoate and dinitrosobenzene[241]. Butyl rubber, 50 phr of Hi-Sil 202, glycerol, stearic acid and the chemical promoter were mixed on a mill and the heat treatment was carried out on the mill for a period of 10 to 40 minutes at 300°–310° F. After cooling, sulfur and vulcanizing agents were added. The remarkable effect of this treatment on the physical properties,

TABLE LXIX

EFFECT OF PROMOTED THERMAL TREATMENT ON SILICA LOADED BUTYL COMPOUND

	No heat treatment	Heat treatment 1 phr Dibenzo GMF 20 min at 310° F
Modulus, 300%	255	1025
Modulus, 500%	665	2320
Tensile, lbs/in	2545	3110
Elongation, %	800	640
$\eta f \times 10^{-6}$, poises × cps	6.35	2.34
$K \times 10^{-7}$, dynes/sq cm	10.90	7.79

particularly on dynamic properties measured on a modified Yerzley and on modulus, are shown in Table LXIX[108].

The extra processing operation, involving a long period of time and high temperatures, is an objectionable feature of the thermal treatment with these particular promoters. Later, it was found that similar improvement could be obtained in a normal mixing cycle at conventional time and temperature by using N-methyl-N,4-dinitrosoaniline (Elastopar)[235,236].

Unfortunately, the first three mentioned chemical promoters of thermal interaction cause severe discoloration which cannot be masked satisfactorily even by substantial quantities of titanium dioxide. Elastopar produces a less severe tan discoloration which is not desirable in white or pastel compounds but is not noticeable where stronger colors are used.

I. PRESENT USES FOR REINFORCING SILICA IN RUBBER

In what sort of rubber goods are the reinforcing silicas used today and for what reasons?

1. They are used alone to produce items which must have the highest possible physical properties and which must be made in some color other than black. Where lower quality is acceptable, combinations of 30 to 50 parts of silica with 40 or more parts of precipitated calcium carbonate or clay are frequently used to obtain good quality and reasonable cost.

2. They are used to put a modest amount of quality into cheap, nonblack SBR compounds highly loaded with clay or ground whiting that would otherwise have little tensile or tear strength. This is comparable to using an HAF or FEF black to strengthen a compound highly loaded with MT black.

3. The relatively low modulus and high elongation imparted by hydrated silica, results in excellent flex resistance in silica compounds that also have high tensile strength, tear and abrasion resistance. Good flexing is not always found in highly reinforced compounds. This accounts for an increasing use of silica both alone and in mixtures with blacks in industrial products such as belts and hose where flexing is important.

4. They are used to produce transparent and translucent compounds[237]. No commercially-available fillers other than reinforcing silica are suitable for this purpose.

5. They are used to prevent oil blooming from the newer oil extended polymers which contain 50 parts of nondiscoloring paraffinic oils. These oils are less compatible with rubber than the naphthenic oils and will bleed from the elastomer when it is cured tightly unless a high oil absorption filler, such as silica, is present.

6. They are used where exceptional resistance to gaseous and liquid petroleum fractions is required. Molded neoprene oil well parts are compounded with silica to obtain maximum resistance to gases under pressure[238]. Similarly, it has been found that Hi-Sil loaded nitrile blowout preventers, used in oil well drilling, do not fracture and tear as readily as black compounds.

Typical of the rubber goods having some of the above requirements are the products of the sole and heel industry, one of the larger consumers of silica. Use of silica results in a nonmarking "nuclear" sole that has abrasion, tear and flex resistance properties which were never before obtainable. All of the premium quality nuclear, microporous, high profile, transparent and translucent soling made in the United States contains silica.

High quality rolls, belts and hose that will not smudge the materials they touch are required in many industries such as those that produce paper, textiles and tin plate and in food processing plants. Silica is used in these both for its nonmarking properties and for the improved flexing it imparts.

Reinforcing hydrated silica finds its way into compounds that must have high abrasion resistance and be colored for identification or easy visibility such as wire and cable jackets and some types of hose.

Not many years ago all of the rubber parts in household appliances were black because high quality was not obtainable in mineral-filled compounds. Today, an appliance manufacturer would not think of using funereal black rubber for any visible part. Reinforcing silica permits him to have quality rubber parts in any pastel color he may choose.

Silica is being used in many other items in which both color and good physical properties are essential for consumer acceptance of the goods. These include such things as rubber housewares, printing blankets and engraving gum; molded drug sundries and pharmaceutical items; white hospital sheeting; translucent tubing, pessaries, nipples and similar items; transparent adhesive masses for tapes, can-sealing compounds and neoprene adhesives of various types; gas masks; white, grease-proof boots and aprons for the meat packing and food processing industries; tennis shoes; covers for rubber soccer balls, footballs and basketballs; artifical leather made from SBR and high styrene copolymers; and floor tile.

The possibility of using brightly colored tires on automobiles has been considered by stylists in the automotive industry for some time. Numbers of experimental colored tires have been made with treads of nonstaining SBR 1502 loaded with 50 phr Hi-Sil 233. These tires have been run by an independent testing company in Texas at standard inflation and load, changing position of the tires at regular intervals. The best tire of a recent set was run to smoothness at 54,720 miles. Other tires were removed at lower mileages because of injuries not connected with the fact that they had silica treads. Distance traveled by these tires and tread wear measured in miles per 0.001 inch of tread depth loss is shown below.

Mileage	Miles/0.001 in loss of tread depth
54,720	148
29,700	157
21,660	164
16,426	143
15,400	154

Limited production of colored tires in popular commercial sizes is planned for 1960.

J. FUTURE COMPETITION BETWEEN BLACK AND SILICA

It may well be that the kind of reinforcing fiiller used in tires is about to complete a full cycle—from white to black to white.

Until the end of the last century, rubber men did not even begin to understand the relationship of fillers to the properties of vulcanized rubber goods. At that time they began to appreciate the reinforcing properties of zinc oxide, and for some years it was the principal reinforcing agent used in all rubber goods including tires. Although S. C. Mote and Thomas Sloper, of the India Rubber, Gutta Percha and Telegraph Works Company, Ltd., of Silvertown, England,

had begun experimental work with fine gas carbon black in 1904, and obviously recognized that it was as good a reinforcer as zinc oxide, there was no commercial application of their discovery until after 1910. Before that time, the body of a tire was made of square woven fabric which failed quickly because of the friction between the crossed cords. There was no need for a stronger tread compound and, if one had been used, its better properties would have been wasted. The advent of cord tire construction ended early carcass and sidewall failures and made better treads necessary. The white, zinc oxide treads of earlier years had been good enough for carcasses of square woven fabric but were inadequate for cord carcasses. The English company began regular use of gas black in tires about 1910. In the same year, the Diamond Rubber Company bought the right to make the cord tire in the United States and with it obtained the carbon black tread formula. The rubber industry's shift to carbon black was quickened by the war-time shortage of zinc metal and the consequent scarcity and high price of zinc oxide. By 1920, the white reinforcing agent, zinc oxide, had lost out completely to the black reinforcing agent, carbon black, because the latter was much better and cheaper. Carbon black has from that time reigned supreme as king of rubber reinforcing fillers; there has not even been a potential challenger until recently. Now it appears that we may have come full circle and a new kind of reinforcing white filler, silica, may contend with carbon black for a share of the top position.

With anticipated developments in rubber compounding it is likely that silica will equal or surpass tire black when both quality and cost are considered. That is, a dollar's worth of silica made into tires may give as much or more service than a dollar's worth of black. This can result from a rise in carbon black prices and a continuing decrease of the cost of reinforcing silica. Black prices have held fairly steady for the past decade, although the trend has been upward. Silica prices, on the other hand, have decreased steadily.

It is not reasonable to suppose that the present price trends of the two raw materials will reverse themselves. Consider the raw material position of each product. In the case of reinforcing silica there is no raw material problem. It is made from ordinary sand by chemical treatment. Carbon black is not in such a fortunate raw material position. It is made from natural gas and from aromatic liquid hydrocarbons, the proportions in 1957 being 47.5 and 52.5 per cent respectively. The trend in the carbon black industry obviously is away from gas as a raw material. Prices of gas have risen steadily in the past decade, but this fact can be dismissed as not too relevant to a consideration of future carbon black prices because the black industry can swing more and more to oil as it becomes necessary to do so. The types of liquid fuel suitable for black manufacture are not available in unlimited quantities, however. Therefore, the swing from gas to oil in carbon black manufacture is not necessarily a permanent solution of the black producer's raw material problems.

As already mentioned, there is no fundamental physical or chemical reason why silica can not perform as well as carbon black. From the physical standpoint reinforcing silicas already have an ultimate particle size smaller than HAF black. The relative chemical and physical contributions of fine particle silicas to reinforcement have previously been discussed in Section V.

A fact that is often overlooked should be emphasized at this point. Reinforcement depends not only upon the filler but also upon the elastomer. Not only improvements in the silica filler but also changes in elastomers may help to increase still further the quality of silica loaded compounds. Hi-Sil 233 imparts better physical properties (also see Table XXVIII) to polar synthetic rubbers

(e.g., nitrile, chloroprene, chlorbutyl, or carboxylic rubber) than it does to nonpolar rubbers (e.g., SBR). This suggests that it may be possible in the future to design synthetic copolymers specifically for use with silica, and that such a rubber and silica will complement each other. There are indications already that this can happen. For example, in a test run by one of the carbon black companies, a tread made from a copolymer of butadiene and methyl vinylpyridine loaded with Hi-Sil 233 had a road wear index of 118 compared with 100 for HAF loaded SBR 1500 and 90 for HAF loaded methyl vinylpyridine copolymer. In road testing a similar copolymer, a synthetic rubber producer

TABLE LXX

COMPARISON OF HAF BLACK AND HI-SIL 233 AT VARIOUS LOADINGS IN NATURAL RUBBER

Formula	42	43	44	45	46	47
Smoked sheets	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
HAF black	36	54	72	—	—	—
Hi-Sil 233	—	—	—	39	58.5	78
PBNA	1	1	1	1	1	1
Santocure	0.6	0.6	0.6	—	—	—
MBTS	—	—	—	0.8	0.8	0.8
DOTG	—	—	—	1.2	1.2	1.2
Triethanolamine	—	—	—	0.5	2	3
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	2	2	2	2	2	2

Formula	Cure 287° F min	300% modulus	Tensile	Elongation	Duro. A	Tear
42	30	1830	4930	540	54	670
	45	1880	4580	540	54	620
	60	1860	4140	500	53	550
	75	1760	4020	500	54	440
43	30	2900	4320	430	64	530
	45	3070	4130	400	65	660
	60	2730	3980	400	66	490
	75	2850	3890	390	65	550
44	30	—	3300	260	74	450
	45	—	3200	250	74	270
	60	—	3170	240	74	150
	75	—	2960	240	74	150
45	15	980	4580	640	58	660
	30	1010	4510	640	59	640
	45	1000	4460	640	59	600
	60	930	4280	640	59	600
	75	880	4260	640	59	560
46	15	1640	4010	560	70	780
	30	1760	3960	560	72	720
	45	1690	3890	560	73	670
	60	1580	3850	570	74	690
	75	1500	3790	570	73	700
47	15	2000	3840	560	78	730
	30	2120	3860	520	81	740
	45	2130	3820	520	82	760
	60	2100	3730	520	83	720
	75	2060	3750	520	83	720

TABLE LXXI

COMPARISON OF HAF BLACK AND HI-SIL 233 AT VARIOUS LOADINGS IN SBR 1500

Formula	48	49	50	51	52	53
SBR 1500	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
HAF black	36	54	72	—	—	—
Hi-Sil 233	—	—	—	39	58.5	78
Flexamine	1	1	1	1	1	1
Santocure	1.1	1.1	1.1	—	—	—
MBTS	—	—	—	0.75	0.75	0.75
DOTG	—	—	—	1.5	1.5	1.5
Sulfur	1.75	1.75	1.75	2.5	2.5	2.5
Circosol 2XH	5	5	5	—	—	—
Paraflux 2016	5	5	5	—	—	—
Diethylene glycol	—	—	—	2.3	3.45	4.6
Coumarone 100° C m.p.	—	—	—	10	10	10
Stearic acid	1	1	1	1	1	1

Formula	Cure 287° F, min	300% Modulus	Tensile	Elongation	Duro. A	Tear
48	30	330	2180	960	48	370
	45	830	3680	760	48	250
	60	1080	3920	680	53	230
	75	1180	3900	650	53	220
49	30	940	2480	700	56	410
	45	1840	3640	570	58	320
	60	2220	3780	500	62	290
	75	2330	3810	480	63	270
50	30	2040	2660	430	70	320
	45	2980	3390	360	72	250
	60	3350	3560	330	75	220
	75	3560	3590	310	75	220
51	15	460	3510	750	58	280
	30	630	3840	670	60	240
	45	650	3910	620	60	230
	60	670	4030	650	63	230
	75	680	3320	600	63	240
52	15	570	4160	800	65	420
	30	930	4300	660	70	390
	45	1000	4290	630	72	390
	60	1010	4250	620	72	380
	75	1020	4140	620	73	370
53	15	930	3650	690	75	510
	30	1350	3820	590	78	480
	45	1500	3720	560	80	500
	60	1530	3820	540	81	490
	75	1540	3770	540	82	480

found that Hi-Sil 233 imparted abrasion resistance nearly equivalent to HAF black while causing only half as much heat build-up[239].

Development of nonhydrocarbon polymers based on hydrocarbons not commonly used in which silica will outperform carbon black is more than a possibility. There are already at least two types of elastomeric materials in which this is exactly what happens. One of these is silicone rubber in which carbon black

has little utility. Another is fluorocarbon rubber such as Kellogg's X-300. The pure-gum tensile strength of the latter rubber when vulcanized with triethylene tetramine is about 1200–1500 psi. Either silica or carbon black will raise the tensile strength to 2500, but where the pure-gum or silica loaded compound will vulcanize in 16 hours, carbon black retards so badly that 65 hours are required for vulcanization. A Hi-Sil coated with silicone oil has imparted tensile strengths of 3900 psi to this particular elastomer.

The physical and chemical similarities and differences between HAF carbon black and a reinforcing silica in the same price range have been discussed in detail[220,229].

The stress-strain properties of vulcanizates containing hydrated, reinforcing silica differ from those with HAF carbon black. Silicas impart higher elongation and lower modulus together with higher hardness which is an unusual com-

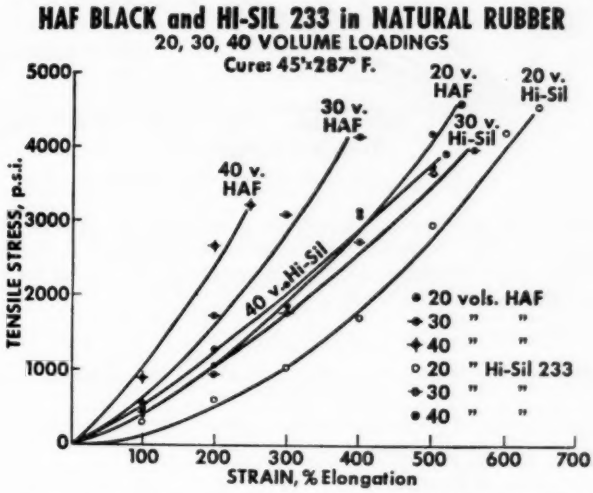


FIG. 26.—Stress-strain curves for HAF black and Hi-Sil 233 loadings in NR.

bination of properties. A comparison of the two materials in natural rubber at 20, 30 and 40 volume loadings is shown in Table LXX[229]. Stress-strain curves of the six compounds drawn from the data in Table LXX are shown in Figure 26.

A similar comparison of the two materials in SBR at 20, 30 and 40 volume loadings is shown in Table LXXI[229]. Stress-strain curves of these six compounds, shown in Figure 27, bear the same relationship to each other that the curves for natural rubber do.

The relatively low modulus and high elongation imparted by silica is probably the reason for the excellent flex resistance of silica compounds having high strength properties, as mentioned earlier. Not only are these properties of interest in industrial rubber goods such as belts and hose, as already mentioned, but also in tire treads because they may help reduce cracking in the tread grooves.

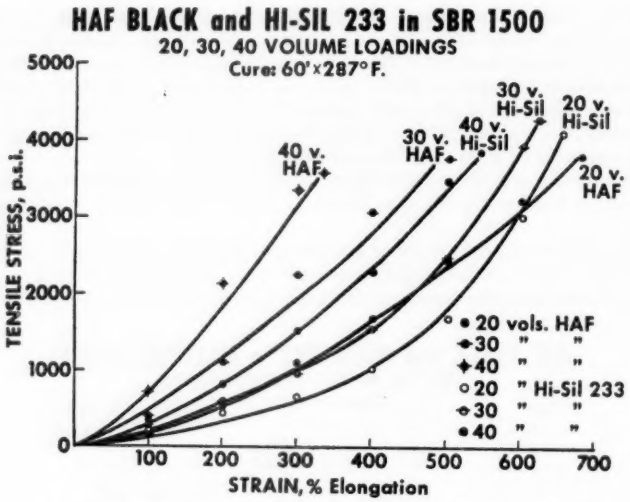


FIG. 27.—Stress-strain curves for HAF black and Hi-Sil 233 loadings in SBR.

The answers to many problems are neither all black nor all white but a certain amount of each. Perhaps the answer to reinforcement of rubber is the same; that is, that the best properties are not obtained from all black nor all white but from a mixture of the two.

TABLE LXXII

COMPARISON OF CARBON BLACK–SILICA MIXTURES WITH CARBON BLACK IN NATURAL RUBBER

Formula	54	55
Smoked sheets	100	100
Zinc oxide	5	5
HAF black	50	30
Hi-Sil 233	—	21.6
Flexamine	1	1
PBNA	1	1
Sulfur	2.5	2.5
Santocure	0.5	0.62
DOTG	—	0.48
Triethanolamine	—	0.2
Stearic acid	3	3

Formula	Cure 287° F min	300% Modulus	Tensile	Elongation	Duro. A	Tear
54	15	2300	4100	490	63	700
	30	2770	4140	430	66	750
	45	2780	4090	420	66	640
	60	2700	3890	410	67	530
55	15	2110	4370	530	62	810
	30	2250	4200	490	64	770
	45	2200	4180	500	64	640
	60	2050	4070	500	64	630

What happens when the rubber technologist uses a mixture of reinforcing black and reinforcing silica? Part of the answer is given in Table LXXII[229]. Modulus is decreased and elongation is increased. Hardness drops a point or two. Tensile strength and machine tear resistance are, if anything, slightly increased. Compounds containing mixtures of the two fillers have a much "knottier" hand tear than the all-black stock.

Some of the reasons why reinforcing silica is being considered now for use in black tires may be summarized as follows:

1. The availability of reinforcing silica is the best insurance the rubber industry has today against future high cost or future scarcity of carbon blacks. Until a practical, reinforcing silica appeared, the tire industry was in the position of having to pay any price asked for carbon black. Reinforcing silica has set a definite ceiling on carbon black prices.

2. Use of silica as a partial replacement for carbon black makes possible a saving in the cost of tread compounds.

3. Compounds containing mixtures of carbon black and silica have better resistance to hand tear than straight carbon black stocks[240,241]. This may make it possible to develop compounds with better resistance to chipping and cutting.

4. The comparatively low modulus of silica compounds may contribute to a decrease in groove cracking. This is of particular interest in compounds for wire tires.

5. Adhesion of many rubber compounds to metal is improved by addition of some silica. Use of mixtures of carbon black and silica may result in improved undertread, breaker and carcass compounds for wire tires and tires with wire breakers.

6. Use of a high oil absorption filler, such as a reinforcing silica, may be useful in treads made with oil-extended polymers to prevent bleeding of the oil into the body of the tire with a subsequent deleterious effect on the adhesion of the carcass compound to the cord fabric.

7. Use of silica in a copolymer of butadiene and 2-methyl-5-vinylpyridine results in a tire tread that gives road wear equal to present first line black treads without producing as much heat in service. This combination of properties is of interest in racing tires and heavy duty truck tires in spite of the high price of this synthetic rubber.

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THE MELTING OF CRYSTALLINE POLYMERS

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I. INTRODUCTION

Polymer molecules are characterized by the unique structural feature of being composed of a large number of chain units covalently linked together. Despite this complexity of structure macromolecular systems still retain the ability to exist in different states, a property common to all substances. Two of the states of matter observed for monomeric substances, the liquid and crystalline states, are also found in polymeric substances. The liquid or amorphous state is characterized by the fact that, because of the freedom of rotation about the bonds connecting the chain atoms, a single polymer molecule can assume a large number of configurations. In this state, therefore, the chain units of different molecules are arranged in a random, disoriented array uncoordinated with one another. Under appropriate thermodynamic conditions, however, a spontaneous ordering of portions of the chain molecules can occur, and in contrast there results a state of configurational order, the freedom of rotation being lost. This latter state is termed the crystalline state.

Major attention in this review is directed to the consideration of the transformation from the crystalline state to the liquid state. Certain closely related subjects as the morphology and organization of the crystalline state[1-3] and the mechanisms and kinetics of crystallization from the melt[4] have been recently reviewed and hence will not be considered in any great detail. The melting process that occurs in various types of polymeric systems will be considered and conclusions drawn from the presently available evidence. Presentation from a unified point of view, based on certain fundamental considerations, is aimed for. The basic underlying principles which govern the phenomena will be stressed; experimental results which demonstrate these principles or point out the need for new developments will be presented. An effort will be made to

consider problems from the point of view of theoretical expectations and experimental findings. On the other hand, no effort is made to include a description of all work in this field, although care has been taken to be as comprehensive as possible in discussing the basic principles.

It has become increasingly apparent in the last few years that many of the basic principles by which the crystallization and melting of synthetic polymer systems can be understood apply equally well to protein systems. Many of these macromolecular systems occur naturally in the crystalline state and it is therefore not surprising that many of their functions and properties are explicable on the basis of a crystal-liquid transformation. For this reason reference will also be made to this type of crystalline macromolecular system.

A wide range of possibilities exists in the way that the individual chain units can be put together to form the macromolecule. They can, for example, be composed of identical units linked together in a linear array, or be composed of many different types of units. In addition to linear molecules there can also be found branched and crosslinked systems. Because of these unique features of structure the spatial distribution of the chain elements of a polymer system plays an important role in determining its properties, physical, mechanical, and thermodynamic. It would appear almost axiomatic that polymer chains possessing a sufficient regularity of chain elements should be capable of undergoing crystallization. Thus, crystallization has been observed in a wide variety of polymer types. Chain irregularities can be thought to consist of chemically different units, stereochemical or geometrical isomers, units involved in branch points and crosslinks as some typical examples. It is known that a certain amount of chain irregularity can be tolerated with crystallization still ensuing. Many polymers whose chemical formulas indicate that they should be crystallizable, from the above considerations, do not appear to undergo the liquid-crystal transformation very readily. This could be due to the presence of subtle types of chain irregularities in sufficient concentration to retard the crystallization.

However, even if the polymer is structurally regular, conditions must be found which are kinetically favorable for the transformation to occur in order that crystallinity can be detected in the time allotted for observation. Thus, for example, polyisobutylene, a polymer of apparently regular structure, can easily be crystallized by stretching. Until very recently it was thought not crystallizable without the application of an external stress. It has been shown[5,6], however, that crystallinity in polyisobutylene can be induced merely by cooling. At the optimum crystallization temperature several months must elapse before the development of crystallinity can be definitely established. The observation of crystallinity in polymers depends not only in satisfying the structural requirements but there must also be provided kinetically favorable conditions for the transformation to occur. For those polymers thought to be structurally regular the absence of crystallization appears to be primarily a problem in crystallization kinetics.

Wide angle x-ray diffraction patterns indicate that under appropriate crystallization conditions three dimensional order can be achieved in the crystalline regions. Not only are portions of polymer chains constrained to lie parallel to one another but order in directions transverse to the chain axis is also developed. X-ray diffraction, infrared, and thermodynamic analysis show that in addition to the ordered regions characteristic properties of the liquid state are also present. Thus the crystallization process is rarely if ever complete in a polymer system.

Detailed structural studies show that in polymer systems bond angles, distances, and other elements of crystallographic structure appear to be normal when compared to monomeric materials. It is not uncommon to have more than one chain passing through the unit cell, and the chain repeating units can be considered to play a role analogous to that of molecules in the crystals of monomeric organic substances. A wide variety of chain structures have been shown to exist in the crystalline state, depending on the polymer type. These structures range from an extended planar structure such as is found in polyethylene[7], polyisoprene[8], polyamides[9], and the β form of the fibrous proteins[10], to various types of helical arrangements of the chain units relative to one another[11,12]. In proteins and synthetic polypeptides the helical structure observed in the crystalline state is thought to be favored by the presence of intramolecular hydrogen bonds. Structural studies of certain of the synthetic polymers, in which the ability to form hydrogen bonds is absent, indicate that helical conformations in the crystal can be developed solely as a consequence of steric considerations.

In describing the crystalline state, distinction must be made between the cases where crystallinity is developed without the application of any external force so that the crystalline regions are randomly arranged relative to one another in contrast to the situation where a preferential orientation of the crystalline regions exists. The latter situation is developed either as a result of crystallization from a deformed melt or by deforming the already existing crystalline polymer. Studies of the morphology of the crystalline state by various experimental techniques such as electron microscopy, low angle diffraction, light scattering from thin polymer films, and optical microscopy utilizing polarized light show that at all levels accessible to study there is a further organization of the crystalline regions. One current problem of great importance is the development of an adequate description of this organization in terms of the molecular and submolecular units of which it is composed.

From a morphological or structural point of view, it is evident that the crystalline state of polymeric systems is quite complex. This is to be expected both from its polycrystalline character and the fact that the crystallizing entities, the chain repeating units, are not isolated elements of structure but are covalently linked together in molecules comprising many thousands of units. These considerations also lead to the expectation that there should be observed a wide range in the type of order developed, depending on the polymer structure and the crystallization conditions. This turns out to be the case. However, the fact that imperfections are observed and variations in the type of order can be developed, in no way implies that these conditions represent the equilibrium state of the system. If this were so it would be meaningless to consider a crystalline phase in polymers and to systematically investigate the transformation from this state to the amorphous state.

It is well known, however, that if the crystallization is conducted under controlled conditions near the melting temperature or if appropriate annealing procedures are followed, the perfection of the crystallinity developed is substantially improved. Furthermore, it has been widely observed that vast changes in the thermodynamic, physical, and mechanical properties occur as a polymer system transforms from the crystalline to liquid state. Despite the morphological complexities that exist in the crystalline state, and the widespread experimental investigation of these phenomena, the question as to whether a true crystalline phase can be developed in polymeric systems is one

which only appropriate thermodynamic experiments and analysis can answer. It is from this latter point of view that the present review is undertaken.

II. HOMOPOLYMERS

A. BULK SYSTEMS

During the transformation from the partially crystalline state to the liquid state polymer systems incur certain characteristic changes in physical properties, in x-ray diffraction patterns, and in thermodynamic quantities which are very similar to the changes observed during the crystal-liquid transformation of monomeric substances. Thus, for example, the rigidity characteristic of a solid crystalline material is lost on melting, as is the crystalline x-ray diffraction pattern. Both types of systems display latent changes in the enthalpy and volume on melting. Since the melting of monomeric substances is relatively well understood and can be characterized as a first-order phase transition it becomes important to ascertain whether the observed similarities are merely superficial or are actually manifestations of the same fundamental process.

For a pure one-component species at constant pressure, a first-order phase transition is characterized by the fact that the transformation temperature is independent of the relative abundance of either of the phases being maintained in equilibrium. The melting should be infinitely sharp and occur at a characteristic temperature, defined as the melting temperature. For this behavior to be observed experimentally would require the perfect internal arrangement of the crystalline phase and the development of crystals of sufficiently large size so that any contribution to the free energy due to the surface between the two phases is negligible when compared to the free energy of fusion. If the above conditions are not fulfilled the melting range will be broadened from that expected theoretically, as the more imperfect and the smaller crystals would melt at lower temperatures. If this situation occurs, the melting range could be narrowed by the adoption of appropriate annealing procedures. However, as has been shown theoretically even a diffuse melting process can still be treated as a first order transition by thermodynamic methods[13].

The polycrystalline character of polymer systems, and the fact that not all portions of a given molecule need participate in the crystallization would be expected to make extremely difficult the establishment of equilibrium between the two phases at high levels of crystallinity. The establishment of this condition would require the development of large and perfect crystals at temperatures far below the melting temperature. Consideration of the crystallization mechanisms as deduced from crystallization kinetics studies points out certain inherent difficulties in establishing equilibrium under these conditions[4]. Thus methods and procedures must be sought by which the crystallinity developed can be improved upon so that conditions more closely approaching equilibrium are obtained. The aforementioned considerations are of major concern when performing and analyzing experiments which are designed to study the course of the fusion and determine the nature of the transition. Experiments designed to yield results of thermodynamic significance must obviously involve the measurement of thermodynamic quantities which are sensitive to small changes in the amount of crystallinity. Unfortunately, these procedures have not always been followed. A vast amount of experimental data have been amassed wherein the course of the fusion and determination of the transformation temperature have been studied by means which utilize changes in morphological or mechanical

properties. Though of importance within themselves, results obtained by these methods are of dubious significance for thermodynamic analysis. Melting temperatures determined in this manner would bear only superficial resemblance to the desired quantities.

One type of thermodynamic measurement which is appropriate for the study of transformations involves the determination of the specific heat as a function of the temperature. A typical set of results for an undiluted homopolymer are those of Wunderlich and Dole[14] for a linear polyethylene, which are illustrated in Figure 1. The specimen studied was allowed to cool slowly from the melt before the measurements were undertaken and is termed annealed by the investigators. The shape of the experimental curve of Figure 1 strongly resembles a λ-type transition characteristic of an order-disorder process. The specific heat rises sharply over a temperature range of about 15–20°, reaches a finite

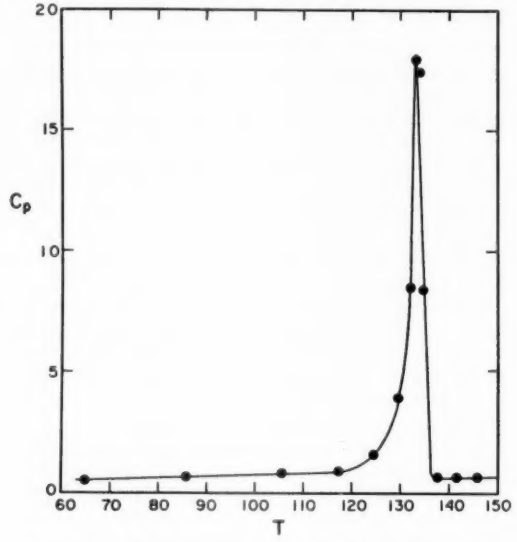

FIG. 1.—Specific heat-temperature relation for linear polyethylene (Marlex-50) from Wunderlich and Dole[47].

maximum value, drops precipitously, and then levels off. Similar curves have been reported for polytrifluorochloroethylene[15] and polyoxymethylene[16]. For an idealized first-order phase transition the curve should go to infinity at the transformation tempreature. It is therefore tempting to conclude that the transformation illustrated in Figure 1 can not be classified as a first-order phase transition.

Mayer and Streeter[17] have, however, discussed in detail the inherent difficulty of classifying a transition by the shape of the fusion curve. The question arises, for example, as to whether the transformation range could be appreciably sharpened by further annealing or adopting a slower heating schedule, or whether a greater rise in the specific heat would be observed at the transformation temperature if the temperature interval of the observation were decreased.

Furthermore, the specific heat-temperature plot for a diffuse first-order transition is very similar in character to that to be expected for a λ-type order-disorder transition[17,18]. Thus the classification of this transition, based solely on the specific heat curve, would be quite arbitrary. A more detailed investigation of the nature of the fusion and the characteristics of the transformation temperature is required.

It is now well known, based primarily on the detailed studies of Wood and Bekkedahl[19] on the crystallization and melting of natural rubber, that if subsequent to the crystallization of a polymer the fusion is carried out utilizing rapid heating rates the melting temperature will depend on the crystallization temperature. These results which are observed in a wide variety of polymer systems[20–22] are explicable on the basis that at crystallization temperatures well removed from the melting temperatures there are morphological contributions which lower the stability of the crystalline regions and which cannot be alleviated when fast heating rates are employed. This suggests that to approach the equilibrium condition crystallinity should be developed at temperatures close to the melting temperature. Since it is usually not practicable to carry out this procedure, it becomes mandatory to adopt an extremely slow heating schedule of about 1–2 degrees per day. This would then allow the polymer full benefit of annealing processes. When such procedures are adopted it is invariably found[21,23–26], if sensitive methods of detection are used, that at a given temperature below the melting temperature partial melting followed by recrystallization occurs. This can be interpreted as indicating the development of more stable crystallites at the expense of the less perfect lower melting ones. The melting points obtained by these methods are substantially higher than those observed when fast heating rates are employed and are independent of any previous thermal history of the specimen. Though admittedly inconvenient, the results of experiment indicate the necessity of adopting these procedures. Data obtained by utilizing fast heating rates after crystallization at temperatures far removed from the melting temperature cannot be used to make an equilibrium thermodynamic analysis of the fusion process.

For most polymers the measurement of the specific volume as a function of the temperature offers a very simple, accurate, and convenient method for studying the fusion process. Most important, it allows for the utilization of slow heating rates and the maintenance of a given temperature for extended periods of time so that partial melting and recrystallization can be studied. Some typical results obtained by this technique when slow heating rates are utilized are shown by the two curves of Figure 2. In this figure there is plotted the final specific volume obtained at a given temperature (after allowing for partial melting and recrystallization) as a function of temperature. The upper curve represents the data for a linear polyethylene similar to that utilized in the specific-heat study illustrated in Figure 1. The specimen had a similar thermal history prior to the initiation of the specific volume measurements. The specific volume of the specimen at 25° was 1.041. This value of the specific volume results solely as a consequence of the mode of crystallization from the melt. As in the case of other polymers, the course of the fusion is marked by partial melting and recrystallization. The melting of the polymer is relatively sharp, as is indicated by the abrupt increase in volume that is observed, about 60 to 70% of the transformation occurring in a 5° temperature interval. The last traces of crystallinity disappear at a well defined temperature which can be taken to be 137.5 ± 0.5°. This temperature is several degrees higher than that determined by the specific-heat method, a fact which can be attributed to the

much slower heating rates utilized in the specific-volume studies[26]. Similar types of melting curves have now been observed for a wide variety of polymers[21,24,27,28].

The lower curve in this figure represents the fusion for the same substance which, however, had initially been crystallized from the melt for 40 days at 130°. This rather rigorous crystallization condition yields a specific volume of 1.018 at 25°, indicating that a higher level of crystallinity and presumably more perfect crystallites have been developed. This is reflected in the fact that a perceptible sharpening in the melting curve is observed for

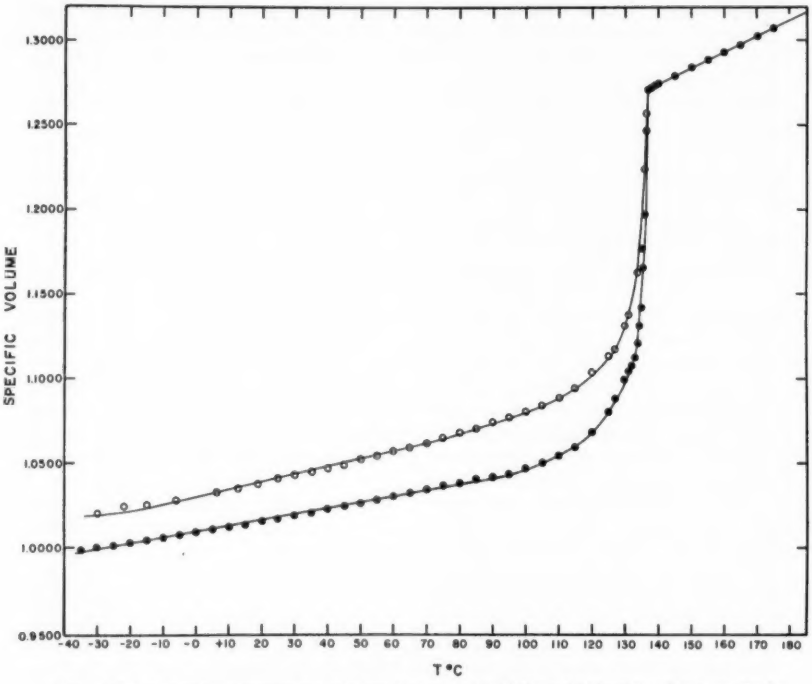

FIG. 2.—Specific volume-temperature relations for linear polyethylene (Marlex-50). Specimen slowly cooled from melt to room temperature prior to fusion, ○; specimen crystallized at 130° for forty days then cooled to room temperature prior to fusion, ●. References 26 and 162.

this specimen, though the last traces of crystallinity still disappear at the same temperature as for the previously described sample. It is therefore demonstrated that by appropriate experiments which involve the adoption of slow heating rates, a well defined temperature exists which represents the temperature at which the last traces of crystallinity disappear. This temperature is independent of the crystallization conditions and previous thermal history of the specimen. Procedures by which the breadth of the melting range can be reduced are indicated. The ultimate limit that can be attained in this respect, from an experimental point of view, is not as yet known. The

answer to this question rests primarily on the patience of the individual investigators since exceptionally long times are required to develop substantial amounts of crystallinity at temperatures close to the melting temperature[4].

Though the melting of homopolymers has been shown to be relatively sharp, the fusion process appears to violate one of the prime requirements of a first-order phase transition of a one-component system, namely that at constant pressure the transformation temperature should be independent of the relative abundance of the two phases in equilibrium. As has been indicated it is not as yet known whether the optimum crystallization and annealing conditions have as yet been developed and utilized. Any improvement in these factors will, of course, sharpen the transformation range. In addition, it must be realized that inherent in any real polymeric system are factors which, by necessity, will broaden the transformation range.

For homopolymers of finite molecular weight at least one of the end groups will differ stereochemically from that of the chain repeating units and will in general therefore be excluded from the crystal lattice. This is similar to the role played by an impurity in the crystallization of monomeric substances and its effect is to broaden the melting range. Thus for polymers of finite molecular weight there will be present always a "built-in" impurity. In addition, the fact that a given chain traverses both the crystalline and amorphous regions precludes the possibility of sharp boundaries being developed between the two phases, even if perfect internal order is developed in the crystalline phase. Some degree of order must persist for a short distance beyond the crystallite ends. This will manifest itself as an effective surface free energy which again will cause a broadening of the melting range. It is therefore possible for a one-component polymer system to undergo a first-order phase transition without adhering to the requirement of an infinitely sharp melting range. The above concepts have been given more quantitative consideration by Flory[29] in his statistical thermodynamic theory of the fusion of polymers

For a homopolymer, uniform in molecular weight at not too high degrees of crystallinity, Flory[29] finds, from calculations utilizing a lattice model for the partially crystalline polymer, that under equilibrium conditions at temperature

$$1/T - 1/T_m^0 = (R/\Delta H_u)[1/x\lambda_e + 1/(x - \zeta_e + 1)] \quad (1)$$

T where T_m^0 is the equilibrium melting temperature of the pure polymer of infinite chain length. This quantity is equal to the ratio of $\Delta H_u/\Delta S_u$, the heat and entropy of fusion, respectively, for the polymer repeating unit. These latter two thermodynamic quantities are characteristic of the polymer chain repeating unit and are independent of the amount of crystallinity in the system. λ_e represents the fraction of the polymer units that are amorphous and x the number of repeating units in the polymer molecule. The equilibrium crystallite length ζ_e is related to the chain length by the relation

$$-\ln D = \zeta_e/(x - \zeta_e + 1) + \ln [(x - \zeta_e + 1)/x] \quad (2)$$

where in the parameter D there is included the effects of the surface free energy of the crystallite ends. The fact that the equilibrium crystallite length is independent of the degree of crystallinity is a consequence of mathematical approximations that were employed in the development[29].

For the stable crystalline phase to exist it is required that the parameter D must assume a value less than unity. Equation (1) indicates that even for a

polymer of uniform molecular weight fusion will occur over a finite range of temperatures, in contrast to that expected for the fusion of a pure monomeric crystal. The temperature interval of fusion will decrease as the molecular weight is increased. The physical reasons for this behavior have already been discussed, and these theoretical considerations give a basis for the observation that for polymers of finite molecular weight the transformation temperature is not independent of the relative amount of each phase. For polymers of non-uniform molecular weight, which correspond to most cases studied, the melting range would be expected to be further broadened. These conclusions are therefore in accord with the observations illustrated in Figure 2, for it is well known that this polymer (Marlex 50) is quite polydisperse, so that the breadth of the melting actually observed is to be expected. On the other hand, for polymers of very high molecular weight where the assumption can be made that $x \longrightarrow \infty$ it is theoretically expected that the range of fusion will depend solely on the departure from perfect crystallinity and hence will depend on kinetic factors governing the crystallization process[29]. In the theoretical limit of a homogeneous very high molecular weight polymer forming a perfectly ordered crystalline state the transformation should occur sharply at a well defined temperature.

Despite the fact that the melting of a homopolymer will occur over a finite temperature range, according to Equation (1) as λ_c approaches unity $(\partial\lambda_c/\partial T) \neq 0$ so that the last traces of crystallinity will disappear at a well defined temperature; above this temperature $(\partial\lambda_c/\partial T) = 0$. As has been noted, this deduction is also confirmed by experiment, and according to the dictates of thermodynamic theory this temperature is defined as the melting temperature T_m of the polymer. It represents the melting temperature of the hypothetical macroscopic perfect crystal. It is noteworthy that in the case of linear polyethylene this temperature, $137.5 \pm 0.5°$ corresponds very closely to the melting temperature extrapolated for a high molecular weight n-paraffin from an analysis of the thermodynamic data for its low molecular weight homologs[26, 30, 31]. We therefore conclude that the transformation of the partially crystalline polymer of finite molecular weight possesses the characteristics of a first-order phase transition and therefore must be treated as such. This is contrary to the conclusion reached by some investigators based solely on morphological considerations[32, 33]. It remains for further experimentation to decide as to whether there is any limit to the level of crystallinity at which equilibrium between the two phases can be developed and maintained.

From the statistical thermodynamic theory[29] there are also derived expressions for the dependence of the equilibrium melting temperature on molecular weight. For homogeneous polymers

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(1 + b)/x \tag{3}$$

where $b = [1 - (\zeta_e - 1)/x]^{-1}$. Thus, except for polymers of extremely low molecular weight, T_m, the temperature at which the last traces of crystallinity disappear, should be independent of molecular weight. This is found to be the case[34]. For polymer possessing a "most probable" molecular weight distribution

$$1/T_m - 1/T_m^0 = (2R/\Delta H_u)(1/\bar{x}_n) \tag{4}$$

where $\bar{x}_n$ is the number-average degree of polymerization. Equation (4) has received verification from studies of the polyester, poly(decamethylene adi-

pate) prepared so as to possess the most probable molecular weight distribution[20]. The melting temperatures depend on the number average molecular weight in the prescribed manner. The equilibrium melting temperature even of a sample of low number average molecular weight will, because of the distribution in molecular weights, be characteristic of the disappearance of the longer crystalline sequences, which are generated from the larger molecular weight species.

B. POLYMER–DILUENT SYSTEMS

Since the melting temperature, as defined above, represents the termination of a first-order phase transition it should obey the thermodynamic laws appropriate to such a transformation. A rather rigorous test of the validity of this conclusion is to investigate the effect of an added monomeric second component or diluent on the course of the fusion and on the melting temperature. If a monomeric second component, which is restricted to the amorphous phase, i.e., excluded from the crystal lattice, is added to the polymer it is deduced from statistical theory[29] that the melting range should be appreciably broadened. The relative amount of broadening will depend on the amount and type of diluent that has been added. Qualitative confirmation of this fact has been reported for a wide number of polymer-diluent systems[21, 24–28].

By adopting the view that we are dealing with a first-order phase transition, quantitative predictions can be made as to the effect of the added diluent on the equilibrium melting temperature of the system. The problem is identical to that of the equilibrium between two phases of a two component system, with one component being restricted to one of the phases. The polymer repeating unit is considered to be one component, while the diluent is restricted to the amorphous phase. Utilizing the Flory-Huggins[35, 35] expression for the free energy of mixing of the two components in the liquid phase and assuming that the ratio of the heat to entropy of fusion per repeating unit is independent of temperature the following expression is obtained for the variation of the melting temperature with added diluent:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \tag{5}$$

where T^0_m is the melting temperature of the pure polymer, T_m that of the polymer-diluent mixture, V_u and V_1 are the molar volumes of the polymer repeating unit and diluent respectively, v_1 is the volume fraction of the diluent and χ_1 represents the polymer-diluent interaction free energy. This equation is, of course, similar to the expression for the depression of the melting temperature of a monomeric binary mixture. According to Equation (5) the melting point depression will depend on the volume fraction of diluent added and on its interaction with the polymer. With other quantities being equal, a larger depression of the melting point should be observed with a good solvent (smaller values of χ_1) than with a poor one. The size of the diluent molecule also affects the melting temperature, the depression being predicted to be greater for diluents of smaller molar volume. The larger the value of ΔH_u, the heat of fusion per mole of repeating unit, the smaller is the expected melting point depression. It should be noted that ΔH_u represents the heat of fusion per mole of repeating unit and should not be confused with the heat of fusion obtained from calorimetric measurements which, of course, will depend on the amount of crystallinity initially present in the system.

This type of analysis could obviously be extended to allow for the case

where the diluent can enter the crystalline phase. This would correspond to the two phase equilibrium of two components both components being present in either phase. This modification, with its additional complexities in analysis and experiment, does not appear to be warranted for most synthetic polymer systems. However, it would appear to be a necessary consideration in analyzing the analogous phase equilibria problem for proteins and nucleic acids particularly in aqueous systems[37, 38]. X-ray diffraction studies have indicated that for the latter type of macromolecules water enters into the crystal lattice.

Equation (5) provides a quantitative basis for further testing of the ideas that have been developed in regard to the fusion process. As has been indicated, at the same composition different types of diluents will affect the melting temperature in different ways. In Figure 3 there is illustrated the effect of diluent types and of composition on the melting temperature of a linear polyethylene[26]. The two lower curves represent the melting temperature composi-

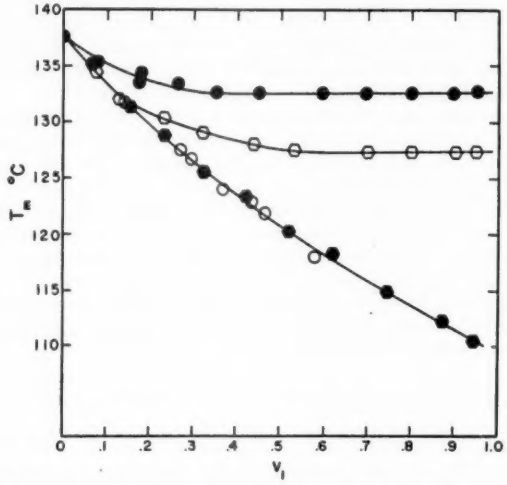

FIG. 3.—Plot of melting temperature-composition relations for linear polyethylene (Marlex-50) for different diluents. *n*-butyl phthalate, ●; *o*-nitrotoluene, ◯; α-chloronaphthalene, ◒; tetralin, ○. v_1 is volume fraction of the diluent present in the mixture. Reference 26.

tion relations when tetralin and α-chloronapthalene are employed as diluents. A continuous decrease of the melting temperature is observed as increasing amounts of diluent are added, as would be expected for such relatively good solvents. The upper two curves representing n-butyl phthalate and o-nitrotoluene as diluents are of quite different character. With the initial addition of diluent a depression of the melting temperature is observed. However, for diluent concentrations exceeding a critical concentration the melting temperature remains invariant with further dilution. Similar effects have been observed with polychlorotrifluoroethylene[39], poly(N,N-sebacoyl piperazine)[21], and branched polyethylene when mixed with appropriate diluents. This phenomenon can be given a simple explanation when it is realized that the molten state for these mixtures consists of two immiscible liquid phases. Thus

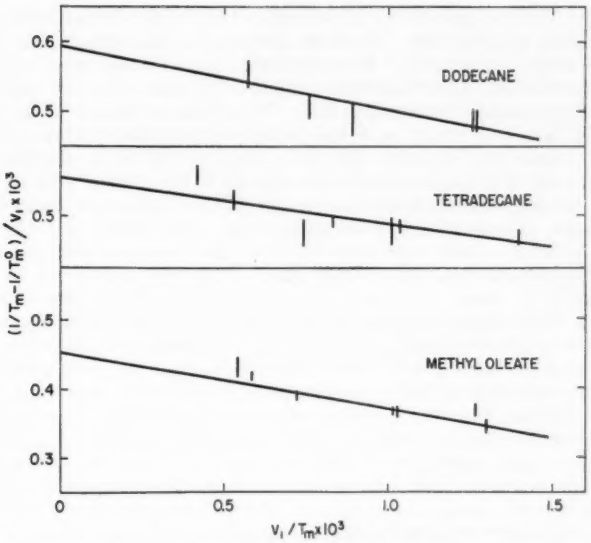

FIG. 4.—Plot of quantity $(1/T_m - 1/T_m^0)/v_1$ against v_1/T_m for natural rubber mixed with indicated diluents. Reference 24.

at the melting temperature three phases coexist in equilibrium, and as a consequence of the phase rule the melting temperature will remain invariant with composition at constant pressure. A further adherence of crystalline polymer systems to the thermodynamic requirements for phase equilibria is therefore observed.

If it is assumed that χ_1 varies directly with the reciprocal absolute temperature, then (with the exception of the invariant region) a plot of the quantity

TABLE I

TYPICAL RESULTS FOR ΔH_u AS DETERMINED FROM EQUATION (5)

Polymer	Diluent	ΔH_u cal/mole of repeating unit
Polyethylene[a,26]	Ethyl benzoate	930
	o-Nitrotoluene	935
	Tetralin	990
	α-Chloronaphthalene	970
Natural rubber[24]	Tetradecane	1040
	Methyl oleate	980
	Dodecane	1100
Polychlorotrifluoro-ethylene[20]	Toluene	1220
	Mesitylene	1100
	o-Chlorobenzotrifluoride	1260
	Cyclohexane[b]	1330

[a] Due to an arithmetical error the values of ΔH_u have been slightly revised from those given in Reference 26.

[b] Data for T_m scatter so that the value of ΔH_u is only approximate.

$(1/T_m - 1/T_m^0)/v_1$ against v_1/T_m for data of the type illustrated in Figure 3 should yield a straight line. From the intercept of this straight line the value of ΔH_u should be deduced. Representative plots of this type are given in Figure 4 for natural rubber and three different diluents. In each case the data are well represented by a straight line. This result is similar to the observations that have been made on a wide variety of polymer-diluent systems[20, 21, 24–8, 39–42]. Since the quantity ΔH_u is a property of the crystallizing chain repeating unit, it is independent of the nature of the diluent used so that the different values of the intercept observed in Figure 4 reflect the different values of the molar volume of the added component. The results given in Table I indicate that for natural rubber the value of ΔH_u deduced from these experiments is independent of the diluent used. There are also given in Table I some additional data for some typical polymer-diluent systems. It can be concluded from experiments on a wide variety of polymer-diluent mixtures that ΔH_u is an inherent property of the chain repeating unit and is independent of the nature of the diluent. The adherence of the observed melting point composition relations to the requirements of Equation (5) offer additional substantive evidence that the crystal-to-liquid transformation in polymers is a first-order phase transition and obeys the appropriate thermodynamic law.

Besides being applicable to synthetic polymers Equation (5) should also describe the melting point—composition relations for protein-diluent systems which satisfy the initial assumptions. This is exemplified by the study of Flory and Garrett[43, 44] for the system collagen-ethylene glycol where it is shown that Equation (5) is obeyed. Experiments of this type, of course, require the measurement of melting temperatures which are of thermodynamic significance, and Equation (5) is valid only when the diluent is excluded from the crystalline phase. This latter condition is not fulfilled for the collagen-water system nor is the measurement of the shrinkage temperature an adequate substitute for the melting temperature. Therefore, it is not surprising that when these conditions exist discordant values of ΔH_u can be obtained for this polymer[45].

In deriving Equation (5) recourse is made to the Flory-Huggins expression for the mixing of randomly coiled polymer chains with monomeric diluent. This is valid for concentrated or moderately concentrated polymer solutions. For dilute solutions, however, the lattice treatment is no longer an adequate description of the binary liquid phase since it does not properly account for the nonuniform concentration of polymer segments in the solution[46]. Thermodynamic theories applicable to dilute polymer solutions must then be used to express the chemical potential of the chain repeating units in the molten phase in calculating the relation between melting temperature and composition. An expression similar in form to Equation (5) results. Adequate systematic studies of the melting point-concentration relation in the dilute range have not as yet been reported so that detailed comparison with theory can not be made.

Equation (5) can also be considered to express the temperature limit of solubility of a crystalline polymer in a solvent. When thermodynamic quantities such as ΔS_u and χ_1 vary with temperature in an appropriate manner, the situation can arise where a negative temperature coefficient of solubility is observed in the dilute region. Thus crystallization will occur on heating, and melting on cooling, in quite an opposite manner to the conventional case. Such systems have been observed; they usually involve highly polar polymers and are typified by the results for the system nitrocellulose-ethyl alcohol recently reported[47].

The melting temperature or solubility of a partially crystalline polymer at a given concentration will not be very dependent on molecular weight except for the very low molecular weight species. Thus the crystallization of a polymer system even from dilute solution will not provide a very effective method of molecular weight fractionation. Not only is the equilibrium transformation temperature not sensitive to molecular weight, but even in dilute solutions supercooling will invariably occur[4]. Thus as the liquid phase is cooled the crystallization of the polymer species will be governed by kinetic processes. Therefore, in order to effectively separate a heterogeneous polymer into its constituent molecular weight species by precipitation from dilute solution, it is necessary to establish the fact that crystallization is not occurring and the polymer is separating out as a liquid phase. This can be accomplished by appropriate phase diagram studies.[48]

Since supercooling of a dilute solution composed of a crystallizable polymer species occurs, and at small values of undercooling the crystallization rate is slow, extreme care must be taken in studying hydrodynamic and thermodynamic properties of such solutions. Since studies of this type are usually interpreted in terms of amorphous polymer chains, the measurements must be made above the melting temperature of the mixture. If this precaution is not taken a partial ordering of the polymer chains can take place. This will of course make the interpretation of the thermodynamic and hydrodynamic measurements extremely complex.

In the discussion of the crystallization of two component systems consideration has been limited to the case where in the liquid phase the polymer molecules can be represented as random coils. In a general sense this is a highly restrictive limitation to place on polymer molecules. For many polymers, such as the synthetic polypeptides and proteins, dissolution can occur with the individual molecules still retaining their asymmetric form[49, 50]. The molecules exist, in solution therefore, in a highly asymmetric rod-like form; this form is presumed to be a result of helical chain conformations being stabilized by intramolecular hydrogen bonds. For non-hydrogen bonded structures, as would be the case for many of the synthetic polymers, a very extended conformation in solution in contrast to the randomly coiled form could result from successive chain atoms assuming a highly preferred configuration. Irrespective of the basis for the individual molecules adopting a highly asymmetric form in solution it has been shown[51], that on account of space filling requirements, such molecular species can exist in random orientation relative to one another only at high dilution. As the solution is concentrated or if the thermodynamic interaction parameter is increased an instability develops in the system so that a concentrated ordered phase will separate. This process is similar to crystallization, and an equilibrium can be established between the solution of the individual asymmetric molecules and the bulk ordered phase[51]. This bulk phase, representing an ordered array of rodlike molecules, can also be transformed under appropriate conditions to the state where the molecules are randomly coiled. It has also been shown experimentally that the rodlike molecules in the dilute phase can also be transformed to random coils[52, 53]. This is akin to a one-dimensional or intramolecular phase transition to which a great deal of theoretical attention has recently been given[54–60]. There exists therefore in the phase diagram of such systems a point at a given temperature and composition where the three phases representing the randomly coiled state, the ordered phase, and the dilute solution of randomly oriented asymmetric particles will coexist[61, 62]. This is similar to the triple point for the coexistence of solid, liquid, and vapor.

III. THERMODYNAMIC QUANTITIES

Since the equilibrium melting temperature of a homopolymer is a well defined thermodynamic quantity susceptible to measurement by suitable experiment, it becomes a matter of interest to determine as to how this quantity depends on the chemical and structural nature of the chain repeating unit. Since the melting temperature is governed by the ratio of the heat to entropy of fusion per chain repeating unit, attention must be focussed on these latter two quantities. Though the required thermodynamic quantities have now been determined for a variety of different polymer types, it would be premature to expect that quantitative laws concerning this problem can be formulated at

TABLE II

THERMODYNAMIC QUANTITIES CHARACTERIZING THE FUSION OF POLYMERS

Polymer	T_m^0, ° C	ΔH_u cal mol^{-1}	$\Delta H_u/M_0$ cal g^{-1}	ΔS_u cal deg^{-1} mol^{-1}	ΔS_u/ bond cal deg^{-1}
Polyethylene[26]	137.5	960	68.5	2.34	2.34
Polyisoprene 1,4 *cis* (natural rubber)[24]	28	1,050	15.3	3.46	1.15
Polyisoprene 1,4 *trans* (gutta percha)[a,25]	74	3,040	45.1	8.75	2.92
Polychloroprene 1,4 *trans*[b,22]	80	2,000	22.6	5.68	1.89
Polychlorotrifluoroethylene[39]	210	1,200	10.3	2.49	1.25
Poly (decamethylene adipate)[27]	79.5	10,200	36	29	1.60
Poly (decamethylene sebacate)[30]	80	12,000	35	34	1.55
Poly (decamethylene azelate)[40]	69	10,000	31	29	1.39
Poly (nonamethylene azelate)[40]	65	10,300	33	30.5	1.52
Poly (decamethylene terephthalate)[40]	138	11,000	36	27	1.91
Poly (hexamethylene terephthalate)[40]	160.5	8,500	34	19.5	1.95
Poly (N,N′-sebacoyl piperazine)[21]	180	6,200	24.5	13.7	1.25
Poly (decamethylene sebacamide)[40]	216	8,300	24.5	17	0.77
Poly (decamethylene azelamide)[40]	214	8,800	27	18	0.86
Cellulose tributyrate[41]	207	3,000	8.1	6.2	3.1
Cellulose trinitrate[42]	700	900–1500	3.0–5.0	1.5	0.75
Cellulose (2.44) nitrate[64]	617	1,350	5.2	1.51	0.76
Cellulose tricaprylate[65]	116	3,100	5.7	8.0	4.0
Polyethylene oxide[28]	66	1,980	45	5.35	2.68
Collagen[44]	145[c]	2,250	24	5.85	1.95

[a] For the higher melting polymorph.
[b] Extrapolated to the all 1,4 trans polymer.
[c] Extrapolated from melting points of diluent mixtures.

present. However, a consideration of these fundamental quantities for the various polymers is instructive and certain salient features of the problem can be developed.

In Table II is a summary of the data presently available. The values for T_m^0 listed are those determined by employing slow heating rates following the crystallization. For all the polymers listed ΔH_u was determined from an analysis of the melting point depression by monomeric diluents utilizing the procedure described in the previous section. Though estimates of this quantity could be made from calorimetric experiments[14, 63] values deduced by this latter

method have not be included, since these measurements are usually carried out using rapid heating schedules and the degree of crystallinity of the polymer must be accurately known. In order to allow for the different sizes of the repeating units, when comparing the value of ΔH_u for the various polymers, this quantity has been divided by M_0 the molecular weight of the repeating unit. The heat of fusion per gram of polymer is given in the fourth column of the table. Dividing ΔH_u by the absolute melting temperature yields the entropy of fusion per repeating unit ΔS_u. In an attempt to develop a rational basis for comparing the entropy of fusion of polymers whose repeating units contain different numbers of chain atoms ΔS_u has been divided by the number of single bonds connecting the chain atoms of the repeating unit. This quantity is given in the last column of the table.

One of the more obvious features of the data in the table is the fact that no apparent correlation exists between the melting temperature and the heat of fusion. Similarly, attempts to correlate ΔH_u with the cohesive energy of the system, calculated by various empirical methods, have not been successful[66–68]. It must be emphasized that both ΔH_u and ΔS_u represent the difference in the enthalpy and entropy between the liquid and crystalline states. Therefore, it is the change that occurs in these quantities on fusion that is of importance, and attention must be given to the properties of both states.

In considering the data for the three hydrocarbon polymers that are listed in the table we find that the values of T_m^0 and ΔH_u determined for linear polyethylene are consistent with those predicted from consideration of the data for its low molecular weight homologs. The *trans* polyisoprene is polymorphic and is higher melting than the corresponding cis polymer. This is also true for polybutadiene and is in accord with observations for the structurally similar low molecular weight substances. Although the melting temperatures for the three polymers listed do vary in relation to the heats of fusion calculated on a gram basis, they are not directly proportional. This indicates that the entropy of fusion must be exerting an influence in the location of T_m. Polypropylene has a reported melting temperature of about 176°[69]. This can be considered to be a lower limit for the melting temperature of the completely stereoregular polymer. Although ΔH_u for the polymer has not as yet been reported, it would not be expected to exceed that of polyethylene. Thus, the higher melting temperature for polypropylene can probably be attributed to the contribution of the entropy of fusion.

Three polymers commonly considered to be elastomers are natural rubber, polyisobutylene, and polydimethylsiloxane possess melting temperatures of 28° C[24], 5° C[6], and about −40° C[70], respectively. Though not as yet determined, the heat of fusion for polyisobutylene would be expected to be typical of the hydrocarbon polymers, while the corresponding quantity for the dimethyl siloxane polymer would not be expected to be any lower. The cause for the relatively low melting temperatures for these polymers must reside in the contribution due to the entropy of fusion.

The halocarbon polymers give examples of high melting temperatures accompanied by very low heats of fusion. This is exemplified by the data given in Table II for polychlorotrifluoroethylene. In addition, polytetrafluoroethylene has a melting temperature reported to be in the vicinity of 330° C. Estimates of the heat of fusion, based on studies of the variation of the melting temperature with hydrostatic pressure yield a value less than that for polyethylene[71]. This again indicates the significant role played by the entropy of fusion.

When considered on a weight basis, both the aromatic and aliphatic polyesters have comparable values for ΔH_u. For the aliphatic polyesters containing odd-membered units ΔH_u is slightly less than that for the even-membered polyesters, which could be the basis for the lower melting temperatures that are observed. The aromatic polyesters are much higher melting than their aliphatic counterparts as a consequence of their lower entropy of fusion per repeating unit. However, when considered on the basis of the entropy of fusion per single bond the values for the aromatic polyesters are slightly greater than those for the aliphatics. This would indicate that when the chain backbone contains ring structures the method suggested for comparing the entropy of fusion of different polymer types is not too quantitative. It has been noted[67] that the introduction of ring structures into the polymer chain gives rise to higher melting temperatures, as illustrated by polyesters[72] and polyanhydrides.[73]

Two of the three polyamides for which data are available are capable of forming intermolecular hydrogen bonds while poly(N,N′=sebacoyl piperazine) cannot. The heats of fusion, on a weight basis are, however, comparable for these polymers.* A comparison of the data for the aliphatic polyamides with the corresponding polyesters indicates that despite the much higher melting temperatures of the polyamides their heats of fusion are smaller. Attention is again focussed on the importance of the entropy of fusion and one can assert that the aliphatic polyamides are higher melting because they possess a lower entropy of fusion. Any significance that is to be applied to the role of the hydrogen bonded structures in causing the higher melting temperatures must be reflected in its effect on the entropy of fusion.

For the high melting, highly polar derivatives of cellulose, one notes that these polymers are characterized by low heats of fusion. On a weight basis these values are the lowest recorded for polymers. Significantly, one has in cellulose trinitrate the highest reported melting temperature. Thus, effects of polarity and chain structure must again be reflected in the entropy of fusion. The decreased melting temperature of cellulose tricaprylate with respect to cellulose tributyrate is accompanied by an increase in the entropy of fusion, which can be attributed to an additional gain in the configurational entropy of the ester side groups.

Polyethylene oxide[28] and polypropylene oxide[74] possess almost identical melting temperatures. The introduction of the methyl side group either does not affect ΔS_u and ΔH_u, or if alterations occur in these quantities they do so in the same proportion. However, in the case of polyoxymethylene (poly(methylene oxide)) the melting temperature is substantially increased, and a value of 180° has been recently reported[16]. The thermodynamic basis for this high melting temperature would be a matter of interest.

To date the only protein for which the fusion process has been analyzed to yield the appropriate thermodynamic quantities is collagen. The investigation of Flory and Garrett[44] has shown that the thermodynamic parameters deduced for this polymer are quite similar to those which characterize other polymer systems. Both the heat and entropy of fusion appear to be normal, the heat of fusion on a weight basis being very similar to that of the synthetic polyamides. Any enhanced stability that is given to the crystalline state by hydrogen bond formation is not in evidence, unless this contribution is much smaller than believed.

* It has recently been reported[95] that ΔH_u values for polycapromide and poly(hexamethylene adipamide), as determined by the diluent method, are the same, and equal to 34.8 cal/g. However, only a single diluent was used for each of the polymers, 6-caprolactam, which cannot be considered a judicious choice. In addition, the melting temperatures were determieed by the penetrometer method so it is extremely difficult to assess the significance of the deduced value of ΔH_u.

From this consideration of the thermodynamic parameters that have been measured for various polymers, it becomes evident that the entropy of fusion per repeating unit is of prime importance in establishing the value of the melting temperature. This is particularly emphasized by the data for the very high melting polymers where a relatively low value of ΔS_u is invariably observed. It is a matter of interest to inquire as to whether a molecular interpretation exists for these observations. ΔS_u is a measure of the entropy difference of a chain repeating unit between the crystalline and liquid states so that the effect of both these states must be assessed.

Crystals can be disordered and the extent of any departure from regularity in the crystalline state will alter the entropy of fusion. The amount of disorder would be expected to increase with increasing temperature, which in turn will lead to a decreased entropy of fusion with increasing melting temperature. It has been noted[75–77], for example, that certain of the polyamides undergo polymorphic transitions from triclinic to hexagonal form at elevated temperatures. This latter form will permit a greater amount of rotational freedom in the lattice. It has been suggested[40] that this phenomenon accounts in part for the higher melting temperature of the aliphatic polyamides as compared to those of the aliphatic polyesters since the polyesters do not exist in the hexagonal form. An assessment of the validity of the general tenet that increased configurational disorder in the crystalline state is characteristic of the higher melting polymers must await a more detailed crystal structure analysis in the vicinity of the melting temperature than is at present available[77], as well as a determination of the necessary accompanying thermodynamic data.

On melting, an increase in the configurational entropy of the system must occur because of the vastly different structural characteristics of the two states. In the liquid state polymer molecules can assume a wide array of conformations, which depending on the polymer type, can range from that of random coils to elongated rodlike molecules. The conformations assumed will depend on the specific nature of the chain repeating units and the potentials which hinder the rotation of one chain unit relative to another. The configurational entropy of the liquid state and its contribution to the entropy of fusion will depend on the conformation and relative extension of the individual molecules. A large variation in the entropy of fusion among different polymers can therefore be expected on this basis.

It is known from appropriate dilute solution measurements that in the liquid state natural rubber[78], polyisobutylene[79], and poly(dimethyl siloxane)[80] exist in a highly coiled, flexible form. They are also low melting polymers primarily as a result of entropy considerations. The high entropy of fusion of these polymers could easily result from the large number of configurations which are available in the melt to such a system. In contrast, the derivatives of cellulose are known to exist in a relatively extended form in the molten condition[81–84]. This would tend to decrease the entropy in the liquid state and higher melting temperatures should result. A similar consideration of the data available for other polymers tends to support the concept that the configurational entropy in the melt and hence the entropy of fusion is related to the conformation assumed by the individual polymer chains.

In order to evaluate the magnitude of the configurational entropy gained on fusion one must separate from the observed entropy of fusion the contribution made by the change in volume that occurs on melting. Though the required procedures to accomplish this are well known[85, 86] the necessary data required to perform the calculation are available for only a few polymers. For natural

rubber and polyethylene, where the appropriate data are available, the configurational entropy of fusion at the melting temperature of each polymer is found to be 1.7 and 1.84 cal/deg/mole of repeating units, respectively[24, 26]. This is to be compared with 3.46 and 2.3 e. u. per repeating unit for the total entropy of fusion of the two polymers. Thus, the contribution due to the volume change is significant for both of these polymers and in comparing the configurational entropy of fusion of different polymers it is necessary that this effect be considered. At present the lack of experimental data severely restricts quantitative comparison.

The effect of chain flexibility on the stability of polymer phases has been considered by Flory utilizing a lattice treatment of polymer-diluent mixtures[87]. In this treatment a model for the polymer chain is taken where the bonds connecting the chain atoms are allowed to assume one of two possible configurations relative to the preceding two bonds on the chain. One type of configuration is thermodynamically favored over the other by a free energy difference ϵ due to the hindrance of free rotation of the chain elements about their connecting links. Preferred bond configurations are assumed to lie collinearly with respect to one another, so that perpetuation of the preferred configuration along the chain gives rise to molecules of rodlike shape. A parameter f is then defined as the fraction of the bonds which are in the unfavored or "bent" configuration. According to this model, a chain will be extended or "stiff" when characterized by a small value of f, while for a highly coiled or flexible chain the parameter f will approach unity. The parameter f bears a direct relationship to the quantity ϵ.

Using a lattice of coordination number z which contains the requisite number of sites, the free energy of mixing n_1 pure solvent molecules and n_2 perfectly ordered polymer chains has been calculated[87]. The resulting expression can be separated into two terms only one of which depends on the composition of the mixture. The first of these terms represents the free energy of mixing the polymer molecules without altering their conformation and can be written as

$$\Delta G_M = RT[n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 x n_2 v_1] \tag{6}$$

For the process described by this equation the parameter f is maintained constant. The second term can be written as

$$\Delta G_d = - n_2 RT\{\ln x + \ln (z/2e) + (x - 2) \ln [1/(1 - f)e]\} \tag{7}$$

where f assumes its equilibrium value. e is the natural logarithm base. This equation represents the free energy change incurred when perfectly ordered polymer chains are transformed to the state where the chain elements are randomly arranged relative to one another with the average number of bonds in the thermodynamically favored configuration being given by the quantity $(1 - f)$. Equations (6) and (7) describe the process for mixing perfectly ordered chains and diluent and having as the final state a random mixture where, however, the flexibility of the polymer chain is given by the parameter f.

For a polymer at a given concentration, and chain length z, it is then found that for a sufficiently small value of f the disordered mixture will be less stable than the pure components from which it is formed. Under these conditions the undiluted ordered phase is therefore thermodynamically favored. This situation arises as a consequence of the space filling requirements of stiff chains since in a limited space extended structures can only be packed in an orderly

array. For an undiluted polymer the critical conditions for the stability of the disordered state occurs for values of f equal to or greater than 0.63. Thus according to the model employed, for a one-component polymer system, the stability of the ordered phase is favored when only 37% of the bonds exist in the preferred configuration.

The transformation from the disordered state to the state of parallel arrangement of chains must be a cooperative process and should resemble a first-order phase transformation. If we consider a polymer in the molten state, then as the temperature is lowered the parameter f will increase. When a temperature is reached where f assumes its critical value the spontaneous formation of the ordered state will occur. This transformation takes place solely as a consequence of intramolecular interaction, the role of intermolecular forces not as yet being invoked. The fraction of bonds required to exist in the preferred configuration is surprisingly small.

From this point of view, crystallization or the development of three-dimensional order can be considered to develop as a result of a two-step process. At an appropriate temperature, due to the development of sufficient inflexibility, the one-dimensional ordering process occurs. For homopolymers or polymers possessing sufficient regularity of structural units, only small adjustments in the relative positions of the rodlike molecules are required to bring neighboring substituents into juxtaposition (developing lateral order) and thus completing the crystallization process. The development of lateral order could be accomplished by means of intermolecular forces, so that three-dimensional order should represent the equilibrium conditions. It should be possible to estimate the relative contribution of intra and inter molecular interactions to the relative stability of the crystalline phase by considering jointly the configurational properties of a given chain and the thermodynamic quantities governing the fusion.

According to the theory the latent change in enthalpy that is involved in the intramolecular transformation can be expressed as[87]

$$\Delta H_I = 0.63\,[-\,T^2\partial(\epsilon/T)/\partial T]_p \tag{8}$$

The latent entropy involved in the transformation can be expressed in an analogous manner. Thus to calculate these quantities not only must ϵ be specified but also its variation with temperature. According to the model these quantities are related to the conformation of the individual chains and in principle can be determined from appropriate experiment. In particular the unperturbed-mean-square-end-to-end distance of a chain of x units and bond length l can be expressed as

$$\overline{r_0^2} = xl^2\,(2 - f)/f \tag{9}$$

The ratio of this quantity to the extended length of the molecule r_{max} is

$$\overline{r_0^2}/r_{max} = l\,(2 - f)/f \tag{10}$$

Invoking the critical conditions of inflexibility for the intramolecular transformation to occur gives

$$(\overline{r_0^2}/r_{max})_{cr} = 2.16l \tag{11}$$

A literal interpretation of the theory would require that when the quantity $(\overline{r_0^2}/r_{max})/l$ equals or exceeds 2.16 the intramolecular transformation should

take place. These deductions then focus attention on the conformation of individual polymer molecules as deduced from dilute solution investigations. Solution studies of cellulose derivatives indicate that the conditions of Equation (11) are greatly exceeded at temperatures below the melting temperature. This class of polymers could presumably crystallize by the described mechanism. Studies on polystyrene and polyethylene show that the aforementioned critical conditions are close to being fulfilled and perhaps these polymers also crystallize by the postulated mechanism. A more quantitative assessment of the role played by intramolecular interactions in the crystallization process must await more detailed and complete determination of the required experimental quantities. Of particular importance is the variation of ϵ with temperature, which can be deduced from the variation of f with temperature[87]. The variation of f with temperature can in turn be determined from appropriate experiments by means of Equation (9) or (10).

The theoretical considerations of the properties of partially flexible polymer chains outlined above provide a basis for the molecular interpretation of crystallization and melting. It can be seen, from a qualitative point of view at least, that the entropy of fusion should have an important influence in determining the melting temperature. In addition, the experimental observations that low entropies of fusion and high melting temperatures are characteristic of "stiff" chains receive a natural explanation.

IV. COPOLYMERS

The introduction into a polymer chain of units which are either chemically, stereochemically, or structurally different from the predominant chain repeating element imposes restrictions and limitations on the crystallization process and also on subsequent fusion. For purposes of classification and for the logical consideration of their crystallization behavior, polymer chains which possess nonidentical units can be termed copolymers. In this category we can then consider true chemical copolymers where chemically different groups have been incorporated into the polymer chain as well as cases where stereo and geometric isomers are present. Polymers with other types of chain irregularities can also be included in this description.

When a copolymer crystallizes it is not required, a priori, that the different types of chain elements participate in the transformation. A wide variety of possibilities exists which depend on the crystallization conditions, the sequence distributions of the various units, and the stereochemical relations that exist between them. Although a very frequent situation for synthetic polymers is that in which only the units which occur in major proportion crystallize, cases exist wherein the other types of chain units that are present can also enter into the same crystal lattice. For protein molecules where the constituent polypeptide chains are composed of many different amino acid residues arranged in a specified order the crystallization of all the units appears to occur in certain cases. On the other hand, for other protein systems it has also been tacitly assumed, without any direct evidence, that all the units are involved in the crystallization. This has important bearing on the proper analysis of the melting behavior of this important class of macromolecules. The deduction of the crystal structure of these systems from x-ray diffraction data depends on the knowledge of which specific chain units are involved in the crystallization. The possibility of the nonidentity in composition of the crystalline phase with the overall composition of the polymer must be given serious consideration. In

considering the fusion of copolymers as well as the effect of compositional changes on the melting point it is important that the distinction between the various possible modes of crystallization be made.

Following Flory[29, 88], we consider in detail the case where only one type of unit, designated as an A unit, can participate in the crystallization. For such types of copolymers general theoretical expectations concerned with the nature of the fusion process and the effect of chain composition on the melting temperature are developed. For copolymers adhering to this condition, under equilibrium conditions, the longitudinal growth of crystallites is restricted solely by the occurrence in the chain of the noncrystallizing B units. The extent of the lateral development of a crystallite will be governed by the gain in free energy that occurs as a sequence of A units of sufficient length is added to a crystallite as well as the availability, or concentration, of such sequences in the melt. These concepts can be put in more quantitative terms by the following. Initially in the completely molten polymer, we let P_ζ^0 be the probability that a given A unit is located within a sequence of ζ A units. Then

$$P_\zeta^0 = X_A p^{\zeta-1} \tag{12}$$

where X_A is the mole fraction of A units and p is the probability that an A group in the chain is succeeded by another A group, this probability being independent of the number of A's that may precede the given A unit in the sequence. When crystallization occurs and thermodynamic equilibrium is maintained, the probability P_ζ^e of finding a sequence of ζ A units in the noncrystalline regions is given by

$$P_\zeta^e = \exp\{-\Delta F_\zeta/RT\} \tag{13}$$

where ΔF_ζ is the free energy of fusion of a sequence of ζ units from a crystallite ζ units long. Expressing

$$\Delta F_\zeta = \zeta \Delta F_u - 2\sigma_e \tag{14}$$

where ΔF_u is the free energy of fusion per mole of units and σ_e is the surface free energy per repeating unit at the ends of the crystallite. Crystallites are considered to be of sufficient size so that any contribution of the lateral surface free energy can be neglected. Thus

$$P_\zeta^e = (1/D)e^{-\zeta\theta} \tag{15}$$

where

$$\theta = (\Delta H_u/R)(1/T - 1/T_m^0) \tag{16}$$

and

$$D = \exp(-2\sigma_e/RT) \tag{17}$$

A necessary and sufficient condition for crystallization to occur is that for one or more values of ζ

$$P_\zeta^0 > P_\zeta^e \tag{18}$$

Thus from Equations (12) and (13) we have as the requirement for crystallization to occur the condition that

$$(X_A/p)p^\zeta > (1/D)e^{-\theta\zeta} \tag{19}$$

Since σ_e is a surface free energy and greater than zero, for the condition (X_A/p) less than $1/D$ the inequality (19) becomes

$$\theta > -\ln p \tag{20}$$

or

$$(1/T - 1/T^0_m > -(R/\Delta H_u) \ln p \tag{21}$$

There is, therefore, a limiting temperature above which the inequality (21) can not be fulfilled. Consequently at temperatures above this limiting temperature crystallization can not occur. This temperature is clearly the equilibrium melting temperature T_m so that the inequality (21) can then be written as

$$(1/T_m - 1/T_m^0) = -(R/\Delta H_u) \ln p \tag{22}$$

It is therefore theoretically expected that for a copolymer, only one of whose units can crystallize, the depression of the melting temperature will depend on the heat of fusion per mole of crystallizing unit and the sequence propagation probability p. It should be emphasized that Equation (22) is derived on the basis of thermodynamic equilibrium, which implies that the longitudinal growth of crystallites is impaired only by the occurrence along the chain of the noncrystallizing units and the lateral development is restricted solely by the specified thermodynamic consideration. If other conditions prevail during an experiment, appropriate cognizance must be taken of the departures from equilibrium and of any imperfections that are introduced into the crystalline phase[89].

According to Equation (22) the melting point depression of a copolymer depends not only on the heat of fusion of the crystallizing units but also on the mechanism of the copolymerization as embodied in the parameter p. Thus, if the polymerization kinetics are such that the crystallizing units occur in random sequence distribution, p can be identified with X_A, and Equation (22) becomes

$$1/T_m - 1/T_m^0 = -(R/\Delta H_u) \ln X_A \tag{23}$$

For other cases the problem exists in quantitatively relating the quantity p to the overall composition of the crystallizing units. If there is a strong tendency for the chain units to alternate, p will be less than X_A, and a larger depression of the melting temperature will be expected as compared to the random case. On the other hand, for an ordered or block copolymer where the crystallizing units occur in very long sequences, p will greatly exceed X_A, and the depression of the melting temperature should not be as great. Taking a random copolymer of the hydrocarbon type as an example, to which values of $\Delta H_u = 1000$ cal/mole and $T_m^0 = 400°$ K are assigned, a melting point depression of 61° is calculated from Equation (23) for $X_A = 0.8$; for $X_A = 0.6$ a depression of 115° should be observed. Thus rather large depressions of the melting temperature can easily be expected for a random type of copolymer when compared to the pure homopolymer. Examples of the melting point depressions actually observed in various types of copolymers will be discussed subsequently.

Besides depressing the melting point, the introduction of noncrystallizing chain units also affects the nature of the fusion process. Flory's theory[89] allows a reasonable estimate to be made of the fraction of the units that are crystalline under equilibrium conditions at temperature below T_m and also the variation of this quantity with temperature. The fraction crystalline can be

expressed to a good approximation as

$$w_c = (X_A/p)(1-p)^2 p^{\zeta_{cr}}\{p(1-p)^{-2} - e^{-\theta}(1-e^{-\theta})^{-2} + \zeta_{cr}[(1-p)^{-1} - (1-e^{-\theta})^{-1}] \quad (24)$$

with

$$\zeta_{cr} = -\ln(DX_A/p) + 2\ln[(1-p)/(1-e^{-\theta})]/(\theta + \ln p) \quad (25)$$

where ζ_{cr}, a critical crystallite length, represents the sequence length where the initial concentration and the equilibrium concentration in the amorphous regions are equal.

Utilizing Equations (24) and (25) and considering a hypothetical polymer where $T_m^0 = 400°K$, $\Delta H_u = 10^3$ cal/mole, and $\ln D = -1$, the curves in

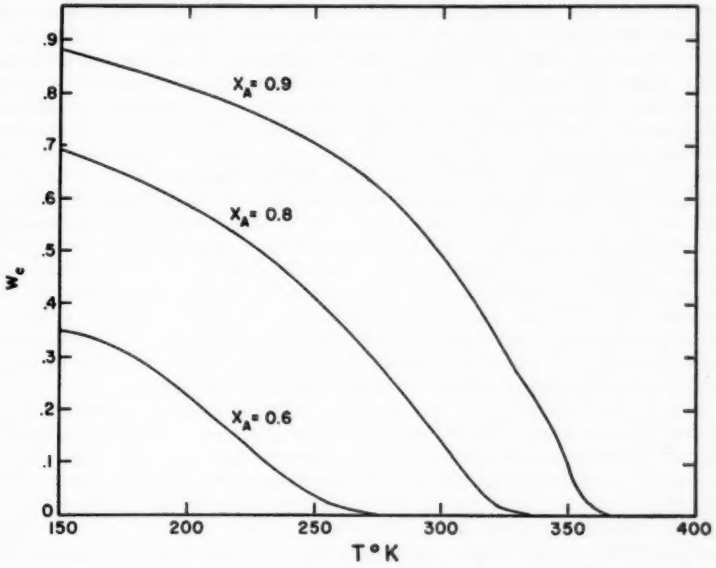

FIG. 5.—Theoretical plot from Equations (24) and (25) of weight fraction crystallinity as function of temperature for random copolymers of indicated composition. $T_m^0 = 400°$ K; $\Delta H_u = 10^3$ cal/mole, and $\ln D = -1$.

Figure 5 have been constructed for random types of copolymers. The plots in this figure represent the theoretical equilibrium degree of crystallinity as a function of temperature for random copolymers containing varying amounts of noncrystallizing units. It is quite apparent that at comparable temperatures the equilibrium degree of crystallinity that can be attained is severely reduced as the concentration of noncrystallizing units is increased. Of major significance is the fact that fusion is expected to occur over a broad temperature range, in marked contrast to that which is expected and observed for a homopolymer of high molecular weight. For polymers of the latter type the transformation is restricted to a very narrow temperature interval.

The diffuseness of the theoretical fusion curves as depicted in Figure 5 does

not in itself appear to be typical of a first-order phase transition. However, the melting range that is expected is a natural consequence of two factors peculiar to copolymers. One is due to the restriction on the size of the crystallites in the longitudinal direction due to the presence of the noncrystallizing units. Crystallites composed of sequences of a smaller number of A units will melt at progressively lower temperatures. In addition, the composition of the crystalline phase and the molten phase are not identical. The overall composition of the melt is dependent on the temperature, with the amorphous regions becoming increasingly richer in A units with increasing temperature. This will also manifest itself in a broad melting range. Thus, despite the fact that the transformation does not occur sharply, the theoretical development indicates that as with homopolymers a first-order phase transition is taking place.

Another significant feature of the theoretical fusion curves for copolymers is the fact that very small amounts of crystallinity will persist for an appreciable temperature interval before the transformation is complete. The breadth of the temperature interval over which this small but significant amount of crystallinity persists increases markedly as the concentration of crystallizing units is decreased. However, the temperature at which all crystallinity completely disappears is well defined theoretically and is identified as the equilibrium melting temperature T_m of the copolymer. For random copolymers T_m will depend on composition in the manner indicated by Equation (23). The curves in Figure 5 indicate that the experimental detection of the melting temperatures that are to be used with Equation (23) will require thermodynamic measurements of great sensitivity. Many of the methods commonly used, particularly those involving morphological changes, are not sensitive to small variations in the amount of crystallinity and hence would be highly inadequate for this purpose. In addition, very careful annealing conditions must be employed in order to develop crystallites which contain long sequences of A units. It is the temperature at which such crystallites disappear which needs to be measured in order to determine the equilibrium melting temperature.

The major conclusions of the theoretical development as embodied in the curves of Figure 5 are in fact substantiated by experiment. It is now well known that copolymers melt over a broad temperature range. In many cases the copolymeric character of the polymer, for crystallization purposes, has not been recognized, and consequently the broad melting has been used as an argument against fusion in polymers being a first order phase transition[90]. On the other hand, detailed study of the melting process is a sensitive method of detecting the presence of chain irregularities in crystallizable polymers.

The melting behavior of the free-radical emulsion polymerized polybutadienes serves as an example of the fusion of this type of copolymer. Though all units are chemically identical, geometrical isomerism exists among the chain units. The concentration of the various isomers can be controlled and altered merely by varying the polymerization temperature. Thus polymers can be prepared which contain varying amounts of the crystallizing *trans* 1,4 units. It has been found that under appropriate conditions crystallization will occur with as little as 55–60% of *trans* 1,4 units[91,92]. In Figure 6 specific volume-temperature plots are given for three polybutadiene polymers with the concentration of crystallizing units X_A ranging from 0.64 to 0.81. Experiments of this type represent a very sensitive method for determining the change in crystallinity with temperature for these polymers. The melting curves are typically sigmoidal, and the transformation occurs over a wide temperature interval. The melting range becomes broader with decreasing concentration

of crystallizing units, while the volume change that occurs on melting also decreases. For the polymer containing 0.64 1,4 *trans* units the change in volume on melting, though detectable, is very small. It is not surprising, therefore, that a popular view has been that a polybutadiene of this composition does not crystallize. The persistence of small amounts of crystallinity at temperatures just below T_m are also observed in accord with theory. This final portion of the melting curve encompasses a larger temperature interval as the concentration of crystallizing units decrease. Thus there is an inherent difficulty for a copolymer containing relatively large amounts of noncrystallizing units to determine the equilibrium melting temperature accurately. In this instance re-

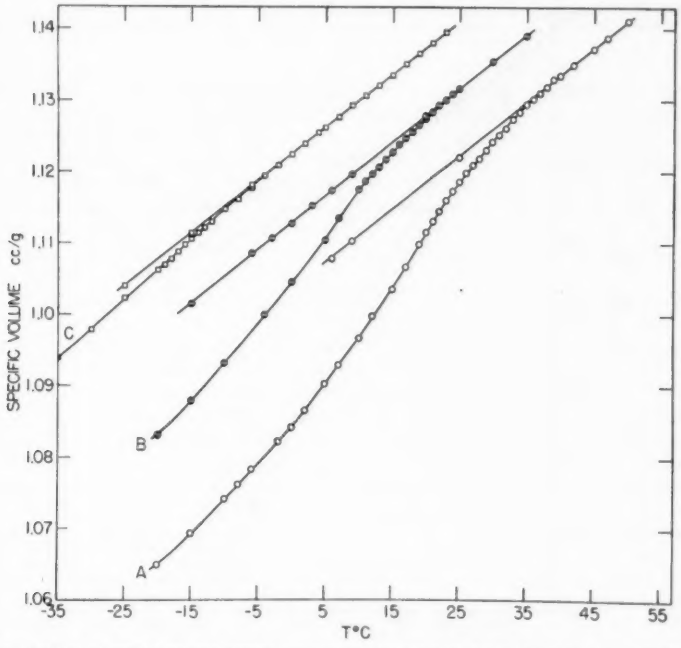

FIG. 6.—Plot of specific volume against temperature for polybutadienes of varying concentration of crystallizing units. For *Curve A*, $X_A = 0.81$; for *Curve B*, $X_A = +0.73$; for *Curve C*, $X_A = 0.64$; *Curves B* and *C* are arbitrarily displaced along the ordinate. Reference 92.

course is made in establishing the supercooled liquidus as an aid in determining T_m. The experimental results of Figure 6 display the major features of the theoretical curves of Figure 5 and can be expected to be typical of the fusion of random copolymers, irrespective of the nature of the noncrystallizing chain units that are introduced.

Copolymers formed by the methods of condensation copolymerization would be expected to be of the random type. Thus copolyesters and copolyamides would be expected to adhere to the concepts set forth above insofar as their melting behavior is concerned. The dependence of the melting temperature of copolyesters and copolyamides on the composition and nature of the

coingredients has received a vast amount of study. Unfortunately, with but few exceptions, the experimental methods used to determine the melting temperature have not been of the kind which would be expected to measure the true equilibrium melting temperature. This is because the sensitivity of the methods is not capable of detecting the last traces of crystallinity which persists for an appreciable temperature interval, and appropriate annealing procedures have not been usually adopted. Despite this basic shortcoming of the

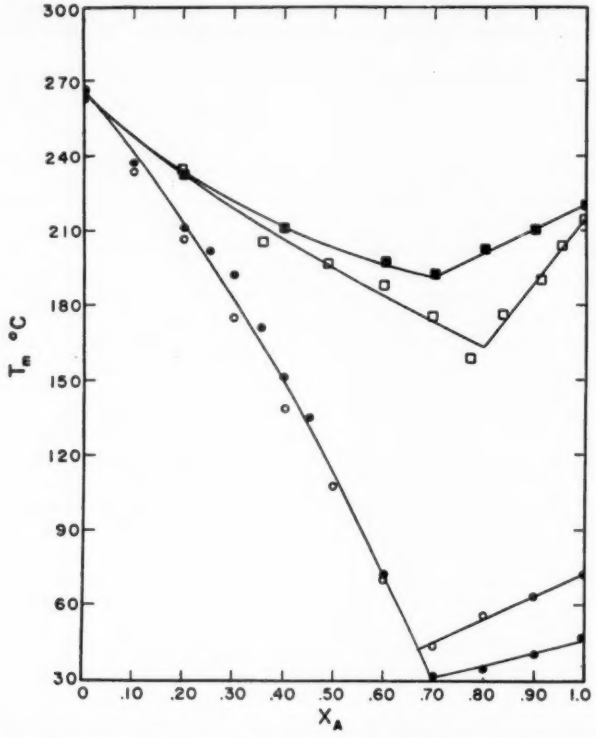

FIG. 7.—Melting temperature-composition relations for various copolyesters and copolyamides. Polyethylene terephthalate/adipate, ●; polyethylene terephthalate/sebacate, ○; poly(hexamethylene adipamide)/sebacamide, ■; poly(hexamethylene adipamide)/caproamide, □. Edgar and Ellery[84], Sonnerskog[163], and Izard[164].

available experimental data, certain qualitative features of interest have been observed. Difficulties in the quantitative interpretation can, however, be anticipated.

In Figure 7 there is a composite plot of the melting temperature-composition relations for some typical copolyesters and copolyamides for which random sequence distribution of the crystallizing units is expected. For copolymers containing ethylene terephthalate and hexamethylene adipamide as the major constituent, the melting temperatures depend only on the composition and are

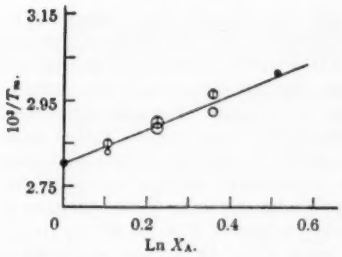

FIG. 8.—Plot of $1/T_m$ against $-\ln X_A$ for decamethylene sebacate copolyesters. Coingredients: decamethylene isophthalate, ⓘ, and cis-1,4-cyclohexamethylene sebacate, ○. Evans, Mighton, and Flory[20].

independent of the chemical nature of the coingredient that is introduced. Wide angle x-ray diffraction patterns[93, 94] indicate that for the crystallization of the ethylene terephthalate copolymers only the ethylene terephthalate units participate in the crystallization. This can also be presumed to be the case for the copolyamides. The depression of the melting temperatures is in qualitative agreement with the predictions of Equation (23). As the concentration of the coingredient is increased, a eutectic-type minimum in the melting temperature is observed with further compositional changes resulting in the crystallization of only the coingredient.

For experiments conducted under suitable conditions such that the requirements of theory are adhered to, the melting temperature-composition relations should be quantitatively described by Equation (23). The functional relation expressed by this equation is obeyed by the data of Figure 7 as well as for other copolyesters[20, 95], copolyamides[20, 21, 95] and for diene type polymers[22, 92] where only one of the structural units is capable of crystallizing. An example of this is given in Figure 8 where the results of Evans, Mighton, and Flory[20] for the melting temperature-composition relations of decamethylene sebacate copolyesters are plotted. The data are well represented by a common straight line for each of the copolyesters which extrapolates to the melting point of the pure homopolymer. Utilizing Equation (23) and the slope of the straight line a value of ΔH_u of 4700 cal/mole of repeating units of decamethylene sebacate is deduced. This is appreciably lower than the value of 12,000 cal/mole determined from studies of the depression of the melting point of the homopolymer by various monomeric diluents. Thus, though the melting points of random copolymers depend on composition in the manner predicted by theory, the

TABLE III[a]

COMPARISON OF THE COPOLYMER AND DILUENT METHODS IN DETERMINING ΔH_u

Polymer	ΔH_u, cal gm^{-1}			
	Copolymer method		Diluent method	
Poly(decamethylene adipate)	13.4	(20)	36	(27)
Poly(decamethylene sebacate)	13.8	(20)	36	(20)
Poly(N-N′Sebacoyl piperazine)	19.8	(21)	24.5	(21)
Poly(decamethylene sebacamide)	23	(20)	24.5	(40)

[a] Data obtained by the penetrometer method[20, 95] are not included in the Table for reasons discussed in text.

values deduced for ΔH_u are usually lower than that determined by other methods. This seems to be the general result as illustrated by the compilation of data given in Table III where for a variety of polymers the value of ΔH_u determined by the copolymer method is less than that determined by the diluent.

Several reasons can be advanced for this observed discrepancy which depend primarily on experimental inadequacies rather than on deficiencies in the theory. The determination of ΔH_u by means of Equation (25) requires the measurement of the equilibrium melting temperatures previously defined. For random type copolymers not only is the melting range broad, but very small though significant amounts of crystallinity persist for an appreciable temperature interval below T_m. As the concentration of crystallizing units is decreased, the temperature interval over which this small amount of crystallinity exists will increase, and since its presence will not be observed by the usual experimental methods an abnormally large melting point depression will be recorded. Since the difference between the observed and true melting temperatures will increase with decreasing concentration of A units, a lower value of ΔH_u, as compared to the correct value, will be deduced. This inherent difficulty in accurately determining T_m even when sensitive methods are used, has already been indicated for the case of polybutadiene, Figure 6, and the diffuse melting behavior has also been reported for copolyamides[21] and copolyesters[63]. Besides the necessity of utilizing very sensitive methods to determine T_m other requirements of theory must also be considered. There must be developed crystallites which are composed of long sequences of A units whose lateral development is restricted only by thermodynamic consideration since it is the melting of such crystallites which determine T_m. This idealized situation can only be approached by adopting rather stringent crystallization and annealing procedures, since various types of imperfections in the crystalline phase can easily be developed which will be more severe as the concentration of noncrystallizing units increases. This will also lead to an abnormally large melting-point depression. Though at present the value of ΔH_u deduced from copolymer melting cannot be considered too reliable it is still a useful parameter in describing the dependence of the observed melting temperature on composition. More detailed experiments designed to approach equilibrium conditions are clearly needed.

Polymers prepared from the 1,3 dienes are subject to chain irregularities due to the geometric and stereochemical isomerism that can exist among the chemically identical repeating units. Thus polyisoprene, polychloroprene, and polybutadiene contain units which can be in the *trans* 1,4 or *cis* 1,4 configurations as well as containing pendant vinyl groups. The naturally occurring polyisoprenes, which contain an overwhelming predominance of groups either in the cis or trans configuration, crystallize readily and their melting is typical of homopolymers. Polychloroprene and polybutadiene prepared by free-radical emulsion methods contain varying proportions of the different units. The composition of the copolymer can be controlled by the polymerization temperature. Sufficient concentration of the *trans* 1,4 units can be developed so that under appropriate conditions crystallinity will ensue. In the case of polybutadiene as much as 40 to 45%[91] of noncrystallizing units can be tolerated without retarding crystallinity. As has been previously indicated, the melting behavior of polybutadiene and polychloroprene is characteristic of copolymers. The melting temperatures of both polymers[22, 92] depend on composition in the manner indicated by Equation (23), so that values of ΔH_u can be deduced. For polybutadiene the melting temperatures of the *trans* 1,4 homopolymer that

is extrapolated from these data[92] stand in good agreement with that directly determined by Natta[96] for the homopolymer prepared by a different polymerization method.

The polymerization of isoprene by free-radical methods does not allow for the development of sufficient concentration of units in either the *cis* 1,4 or *trans* 1,4 configuration for crystallinity to develop. However, by utilizing anionic polymerization methods polymers have been prepared from isoprene in which the units are predominantly either in the *trans* 1,4 or *cis* 1,4 configuration[97–99]. The crystallization and melting of these polymers are very similar to that of their naturally-occurring counterparts, Hevea rubber and gutta percha. However, synthetically prepared *cis*-polyisoprene does not crystallize as readily as the naturally-occurring polymers in the absence of external deformation. Infrared analysis indicates that about 7–10 mole percent of structural irregularities are present in the synthetic polymer[97,98]. If these noncrystallizing units are distributed at random along the chain, then a significant depression of the melting point will be expected according to Equation (23). This will, in turn, lower the temperature at which crystallinity will develop at its optimum rate. It has also been pointed out[4] that due to the kinetic processes involved in crystallization it is more difficult to crystallize a copolymer as compared to a homopolymer at the same values of undercooling. Thus a basis is provided in understanding the reluctance of "natural rubber" prepared synthetically to crystallize readily merely by cooling.

The addition of small amounts of thiol carboxylic acids to naturally occurring 1,4 *cis* polyisoprene severely retards the crystallization rate[100]. It has been reported that concomitantly a portion of the *cis* double bonds are converted to the trans configuration. Thus chain irregularities are developed in much larger proportion by this process than the amount of foreign ingredient introduced. By invoking the same principles as discussed above it is then expected that the transformation will develop at a slower rate when compared with the pure homopolymer at comparable temperatures.

In addition to geometric isomerism another type of isomerism that can exist among the chain elements in certain type of polymers is stereoisomerism. Vinyl polymers to which two different substituents are attached to the alternate carbon atoms are pseudo-asymmetric and the chain units can exist in either the *d* or *l* configurations. Units in which the successive configuration are identical are termed isotactic, while if the units consecutively alternate between the two possible configurations the structure is termed syndiotactic[101]. For polymer chains of this type a wide variety of possible arrangements of the chain elements exists.

After the original synthesis of the crystallizable α-olefins and vinyl polymers which fall into this category, it was thought that they were homopolymers in the sense used here. However, the more general fact of the copolymeric character of these substances has since been recognized[102–105]. Though originally prepared by the methods of anionic polymerization[101, 106, 107], it has since been shown that polymers possessing sufficient stereoregularity to crystallize can also be prepared by a homogeneous free-radical mechanism. For example, by conducting the radical polymerization of methyl methacrylate at a sufficiently low temperature, the addition of units to the growing chain in one configuration is favored over that of the other[102, 108, 109]. This effect of polymerization temperature on the resulting stereoisomerism of the chain is similar to the effect of polymerization temperature on the resulting geometric isomerism that occurs during diene polymerization. Besides the crystallization of por-

tions of chains in either the isotactic or syndiotactic configuration, the crystallization of both types of structure in the same chain has been reported[108]. This is analogous to the crystallization of an ordered copolymer in which both constituents crystallize independently.

Once the copolymeric character of these polymer types is recognized, the appropriate methods by which to treat the crystallization and fusion becomes readily apparent. From consideration of the probabilities that are involved in generating sequences of units in either the isotactic or syndiotactic form Coleman[103] has been able to treat this problem from the point of view of Flory's[88] copolymer crystallization theory. For a polymer of sufficiently high molecular weight, wherein end effects can be neglected, if it is assumed that the probability of addition to the growing chain of a given configuration or type placement is independent of the preceding placement then the statistical problem becomes relatively simple. The quantity p in Equations (22) and (24) can be identified with the probability of a given placement. This quantity in turn will be equal to the fraction of polymer units which exist in this configuration and will be related to the polymerization mechanism, particularly the relative rate of chain propagation. Equations (22) and (24) will then be in the form applicable for copolymers possessing random sequence distribution of crystallizing units, with T_m^0 being the equilibrium melting temperature of either the completely isotactic or syndiotactic polymer.

If these simple considerations do not hold so that the probability of a given mode of addition depends on the structure being offered to the unit being added, that is, on the configuration of the last unit on the growing chain, then the statistical problem becomes more involved. The method of Markov chains is used[103, 104] and one must specify the pertinent conditional probability, as for example, that for an isotactic unit to be followed by another isotactic unit. The relative value of the conditional probabilities determines the tendency for a given type of placement to perpetuate itself. In a formal manner Equations (22) and (24) will still be appropriate when identification is made between the parameter p and the appropriate conditional probability.

Though this formal treatment places the problem in its proper perspective direct comparison with experiment is at present difficult. It is required that the fraction of units in a given type placement, its socalled tacticity, be specified and furthermore the sequence distribution of the crystallizable units must also be known. Even if the simplifying assumption is made that one has a random-type copolymer quantitative comparison cannot be made without knowledge of the concentration of crystallizable units. Though for diene polymers this latter quantity can be determined by spectroscopic methods, general quantitative methods of analysis for stereoisomerism are still being developed.

Despite the problems in analytical chemistry that make difficult quantitative consideration of the fusion process for stereoirregular polymers, experimental results have been reported which allow for a qualitative comparison with theory. These results do give substantiation to the aforementioned concepts. By varying the nature of the catalyst and the polymerization conditions Natta[105] has prepared various crystalline polypropylenes whose melting temperatures range from 176° (presumed to be that characteristic of the pure completely isotactic polymer) to about 106°. These results give strong indication of the introduction of stereoirregularities into the chain. As the melting temperatures of the polymers decreased, the degree of crystallinity that was attained also decreased, ranging from 85% to about 20%. If the crystallinity

was developed under comparable conditions for the different polymers and the equilibrium conditions were approached, evidence is offered for the random nature of the sequence distribution of the crystallizable units. A detailed study of the fusion process for these polymers utilizing controlled crystallization and heating procedures would be very informative.

Certain of the stereoirregular polymers, such as polystyrene prepared by means of alfin type catalysts[10,11] and polymethyl methacrylate prepared under certain specified conditions[107,108], are not obviously crystalline as prepared. However, by treatment with certain solvents at elevated temperatures crystallinity can be induced in these systems[108, 110, 111]. It has already been indicated theoretically and illustrated with various examples that relatively large depressions of the melting temperature can easily be achieved by the introduction of a modest quantity of chain irregularities. For the two cases cited it seems probable that due to the irregular chain structure of the polymer the melting temperature has been depressed from that of the perfectly regular homopolymer so as to bring it into close proximity to the glass temperature. This would make the crystallization process very difficult from the point of view of the kinetics of the transformation. On the other hand, this situation can be alleviated by appropriate solvent treatment. According to Equation (5) the addition of a diluent of large molar volume with poor solvent power (positive χ_1) will result in a further minimum depression of the melting temperature for a given concentration. The depression of the glass temperature when compared with that of the bulk copolymer will depend primarily on composition and not on the nature of the diluent. By adopting this procedure, therefore, the temperature interval between the glass temperature and the melting temperature can be substantially increased over that of the undiluted copolymer. From a kinetic point of view crystallization should then become a more tenable process. This appears to be the explanation for the development of crystallinity in the two cases cited. Though polymer chains may possess sufficient regularity to crystallize, crystallinity will not develop unless kinetically favorable conditions are available. Thus experiments which take full cognizance of crystallization mechanisms must be performed before deciding whether a given polymer can be crystallized.

A similar situation has recently been reported for a copolymer composed of two different chemical repeating units[112]. In a series of dimethyl siloxane-diphenyl siloxane copolymers with the initial introduction of diphenyl type units crystallinity still develops, and the melting point is depressed in the expected manner. However, the glass temperature of the copolymer is also concomitantly increasing. Thus with the addition of from 7 to 15 mole per cent of coingredient crystallinity does not develop in the bulk system because of kinetic difficulties. However, for copolymers containing a higher proportion of diphenyl siloxane the crystallization of these units occurs. Since the melting temperature of this polymer is substantially higher than that of the dimethyl siloxane polymer the temperature interval between the glass temperature and the melting temperature has become sufficiently great so as to make crystallization kinetically favorable.

It has been known that certain polymers, such as poly(vinyl chloride), polyacrylonitrile, polychlorotrifluoroethylene, and poly(vinyl alcohol) are crystalline as usually prepared despite the strong possibility of the occurrence of stereochemical irregularities. In the case of poly(vinyl alcohol) Bunn[113] has pointed out that even if the hydroxyl groups are distributed in random configuration along the chain the spacings of the unit cell are such as to accommo-

date this irregularity. In the case of the usually prepared poly(vinyl chloride), though the x-ray patterns that are obtained do not indicate very well-developed crystallinity, solution properties[114] and mechanical properties[115] give substantial evidence for the development of crystallinity, contrary to certain beliefs[116]. Under polymerization conditions specifically designed to give a more stereoregular structure and with the elimination of branching a more highly and perfectly developed crystalline polymer should be obtained.

From these considerations it is clear that the principles governing the crystallization and fusion of polymers possessing stereoirregularities along the chain are fundamentally the same as those applicable to other types of copolymers. Until analytic methods are developed by which to determine both the fraction of the units in a given configuration and their sequence distributions, direct quantitative studies are seriously hampered. Indirect but valid deductions can be made, however, by careful study of the melting point depression and analysis of appropriately carried out fusion curves. The fundamental question exists as to how does one ascertain by physical measurements when a completely stereoregular polymer is obtained. Studies of the sharpness of the melting process, utilizing thermodynamic methods, should be of great utility in this respect.

The discussion of the crystallization and fusion of copolymers has heretofore been limited to cases where the crystallizable units are distributed either in random sequence distribution or in distributions closely approaching such. Copolymers can, of course, be prepared where these conditions do not prevail. One case of interest is where identical crystallizable units occur in very long sequences. For such an ordered copolymer the sequence propagation probability parameter p of Equation (22) will greatly exceed the concentration of crystallizable units X_A. Therefore, in accordance with this equation the melting temperature for such a copolymer should not be depressed as much as for a corresponding random copolymer of the same composition.

This expectation is borne out by experimental results that have been reported for ordered copolyesters. In Figure 9 there are plotted the results of Coffey and Meyrick[117] on the dependence of the melting temperature of copolymers of ethylene adipate and ethylene sebacate on both the copolymer composition and type. Although the melting temperatures were determined by the penetrometer method so that the results cannot be used for a detailed thermodynamic analysis the dependence on composition should be of qualitative validity. For the random copolymers, the melting point composition relations are similar to that given in Figure 7 for other copolyesters and copolyamides. However, the melting point-composition relation for the ordered copolyesters is quite different and is similar to that for blends of the two homopolymers. For the ordered copolymers it is stated[117] that only the major component crystallizes. The step-shaped melting-composition curve is a consequence of the fact that the parameter p must have a value very close to unity. Thus the introduction into the chain of the second type unit in definite blocks results only in a very slight reduction of the melting point of the polymer, with the reduced melting temperature remaining essentially invariant with composition. Similar effects have been reported by Coleman[118] for ordered copolymers of ethylene terephthalate and poly(oxyethylene glycol). In this case when 30% by weight of the second component is incorporated into the chain only a slight depression of the melting point results.

The distinct possibility exists that the ordered type of copolymer, albeit one extremely more complex, may occur naturally in many of the fibrous proteins.

Besides its general importance, this concept has direct bearing in deducing the structure of these proteins from x-ray diffraction analysis. For example, if only the amino acid residues involved in one type of block are capable of crystallizing it would be only this sequence of repeating units which contributes to the x-ray diffraction. Consequently it is only this structure that is deduced from x-ray studies. Silk fibroin appears to possess an arrangement of amino acid residues along the polypeptide chain which can be considered to be characteristic of a very general type of ordered copolymer. By means of enzymatic hydrolysis, it has been concluded that this fibrous protein consists of blocks of distinctly different types of units[119, 120]. One portion of the chain consists primarily of glycine, alanine, and serine, and it is this portion which contributes to the x-ray diffraction and is the crystalline portion. The other portion of the chain is composed of the amino acid residues containing bulky side groups, and

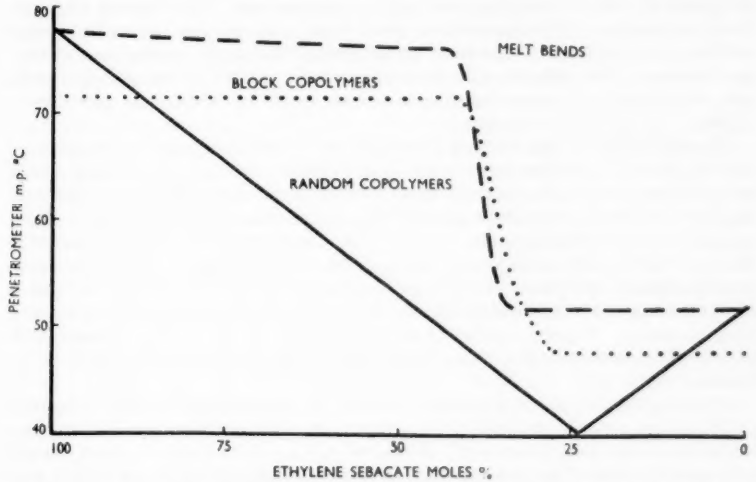

FIG. 9.—Plot of melting temperatures of ethylene adipate/ethylene sebacate copolymers as a function of temperature. Coffey and Meyrick[117].

it is doubtful whether these units participate in the crystallization. A similar type of chain structure can be offered as the cause for the characteristic low angle x-ray diffraction pattern for the fibrous protein collagen, there being a definite periodicity between those blocks which crystallize and those which do not.

When a polymer chain contains two or more different types of units the possibility exists that more than one unit can enter the same crystal lattice. In this instance the units are said to cocrystallize, and x-ray diffraction studies indicate the presence of only one crystal structure. There have now been reported several examples of this type of crystallization[93, 121] and when this situation occurs the melting point-composition relations will differ from that characteristic of either random or ordered copolymers.

Edgar and Hill[93] noted that calculations based on normal bond lengths and angles indicated that the distance between the carboxyl groups in terephthalic

and adipic acid are almost identical. Partial substitution in the crystal lattice of these two diacids might then be expected in appropriate copolymers. This was found to be the case for poly(hexamethylene adipamide)/terephthalamide copolymers. The melting points of the copolymers thus formed increased monotonically with increasing terephthalic acid concentration; no minimum in the curve is observed, as would be expected (see Figure 7) for a random copolymer only one of whose components crystallize. From these results it can be concluded that cocrystallization or isomorphic replacement has occurred in this sytem. On the other hand, replacement of sebacic acid by terephthalic acid in poly(hexamethylene sebacamide) results in a minimum in the melting point composition relations[93] indicating that terephthalic acid does not replace sebacic acid in the crystal lattice. This latter result would, of course, be expected from structural considerations.

Recently Yu and Evans[121] have investigated other comonomeric pairs from the point of view of studying isomorphic replacement. They found that the cocrystallization of the terephthalic and adipic acid residues occurs in copolyamides prepared from a variety of straight chain diamines besides hexamethylene diamine. In addition, they have shown that adipic and terephthalic acids are not unique as isomorphous comonomer pairs in which one member is aliphatic and the other aromatic.

Consideration of the melting point difference between partially substituted and completely substituted derivatives of cellulose indicates the strong possibility of cocrystallization of these units. Wide angle x-ray diffraction studies[122] appear to show that when propylene is copolymerized with ethylene a slight expansion of the crystal lattice in the {110} direction is observed indicative of the fact that methyl groups are entering the crystal lattice. However, since noncrystalline copolymers of ethylene and propylene have been reported[105] it is clear that any cocrystallization of the two types of units must only occur to a limited extent. Careful studies of the dependence of the melting temperature on composition and on the nature of the fusion curve would serve to clarify this matter.

The crystallization of a copolymer from its mixture with a low molecular weight diluent can occur over the complete composition range as in the analogous situation for homopolymers. When crystallized from dilute solution, homopolymers separate into two mechanically distinct phases which are easily separated, as is evidenced for example by the crystallization of polyethylene from dilute solutions in various solvents. On the other hand, when a copolymer crystallizes from a dilute solution a mechanical separation of the two phases can not be made. The crystalline polymer molecules now pervade the whole volume, and the system has been changed from one of relatively high fluidity to a rigid medium of high viscosity. This phenomenon is popularly termed gelation and must be distinctly and clearly distinguished from other types of gel formation as caused by the introduction of a sufficient number of crosslinks into a collection of polymer chains or that which occurs during the polymerization of multifunctional comonomers. Considerable confusion has arisen since gel formation can occur by means of these several diverse phenomena. As considered here, gel formation is limited to the case of the crystallization from dilute solution of a copolymer. This phenomenon has been observed in such synthetic systems as poly(vinyl chloride) in dioctyl phthalate[115], polyacrylonitrile in dimethyl formamide[123], and nitrocellulose in ethyl alcohol[47]. The former two polymers are copolymeric in character because of stereoirregularities among the chain units, while in the incompletely substituted nitrocellulose

cocrystallization of the chain units is probably not complete. It would appear to be a general rule that all polymer systems which display this gelation phenomenon on crystallization are copolymers. The fundamental reason for this resides in the fact that not all the chain units can participate in the transformation. Those chain elements which do not crystallize must prevade the medium, and being interconnected, the noncrystalline units impart to the system its characteristic rigidity and high visocity. The melting of the classical gelation system, that of gelation in water, has recently been shown by Flory and Garrett[44] to be a first-order phase transition.

V. CROSSLINKING

The effect of one type of chain irregularity on the crystallization behavior of polymers which requires special consideration is that in which chain units are involved in intermolecular crosslinks. It has been usually assumed that the introduction of intermolecular crosslinks into a collection of polymer chains has little effect on the melting temperature obtained after subsequent crystallization and fusion. This conclusion was reached on the supposition that if the crosslinked units do not participate in the crystallization they will behave as noncrystallizing copolymeric units[124]. On this basis, for the range of crosslinking usually encountered, it can be calculated from Equation (23) that only a trivial depression of the melting temperature should result. The well known fact that crosslinked systems crystallize from the melt at much slower rates, at a given temperature, in comparison with the pure polymer, has therefore been attributed to restrictions placed on the segmental motions involved in the crystallization by the crosslinkages. Before considering some recent experimental results by which the validity of these conclusions can be assessed, attention must first be given to the crosslinking process and the resultant network formation.

In considering the properties of polymer networks it is customary to assume that crosslinking is a random process, i.e. units of different molecules are paired together in an uncoordinated and random manner[125]. This supposes that not only are the points of crosslinkage randomly distributed in space but also that the polymer chains at the time of crosslinking are in randomly coiled configuration. Though this situation is commonly encountered, these conditions for network formation are restrictive in nature. Networks can also be formed where, though the crosslinks are distributed randomly in space, the chains are in an ordered state when the crosslinks are introduced. It has been shown both theoretically[126] and experimentally[127] that many network properties, including the melting temperature, depend markedly on the chain arrangement at the time of network formation. Thus in considering the effect of intermolecular crosslinks on melting and crystallization it is important that distinction between various types of networks be made.

We consider first the more conventional case wherein crosslinks are introduced at random into a polymer system in which the chain units are randomly arranged in the amorphous state. This corresponds to the usual vulcanization of natural rubber, the irradiation crosslinking of natural rubber at room temperature, and the irradiation crosslinking of polyethylene at temperatures above its melting temperature, to cite but a few examples. Experimental results depicting the dependence of the melting temperature on the fraction of units crosslinked for some typical systems which fall into this category are given in Figure 10. The networks considered in this figure were formed by irradiating

polyethylene above its melting temperature[128] and by vulcanizing natural rubber with either sulfur or *t*-butyl peroxide[129]. Melting temperatures were determined utilizing slow heating rates after the crystallization of the networks from the melt. Plotted in this figure is the observed difference in melting temperatures between the noncrosslinked polymer and the corresponding networks. For the two types of natural rubber networks the melting point depression depends only on the fraction of units crosslinked. As is easily discerned from the data a substantial depression of the melting temperature is obtained for even modest amounts of crosslinking. The melting temperature is depressed 20° when just 1% of the units are involved in crosslinkages. A similar effect is seen for the polyethylene networks formed when the chains are in the amorphous state. For this system a larger depression of the melting temperature is

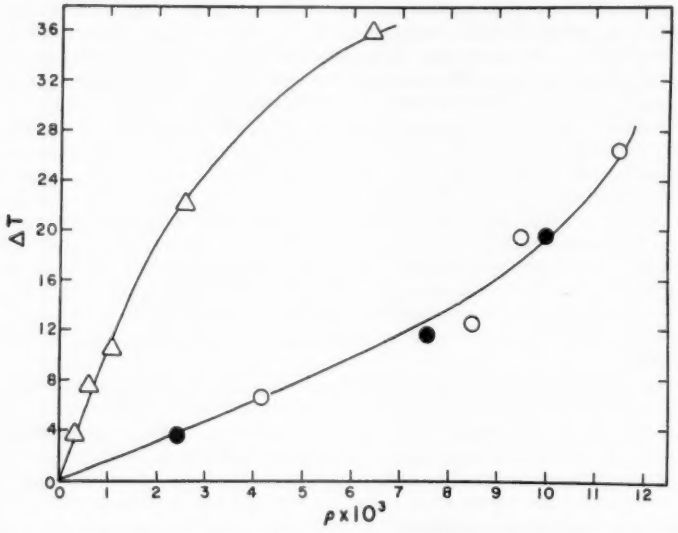

FIG. 10.—Plot of melting point depression (ΔT) as a function of fraction of units crosslined (ρ) for polymer networks formed from random chains. Molten polyethylene crosslinked by ionizing radiation, △; natural rubber crosslinked with sulfur, ○; natural rubber crosslinked with di-*tert*-butyl peroxide, ●. References 128 and 129.

observed when only a small fraction of the methylene units are crosslinked. Thus, the earlier surmise that crosslinking has a negligible effect on the equilibrium melting temperature is not borne out by experiment. In the analysis of the crystallization kinetics of undeformed networks it is therefore mandatory that accurate determination of the melting temperature be made. The adoption of this procedure will enable comparison to be made of the crystallization rates of the network and noncrosslinked polymers at the same value of undercooling. Only when this is done can the influence of crosslinks on segment mobility and its influence on the crystallization process be properly assessed. Price[130] has recently reported that the rate of growth of spherulites in networks formed from amorphous polyethylene depends only on the undercooling, and is independent of the fraction of units crosslinked.

When crosslinks are introduced in a random manner into a collection of polymer chains which are randomly arranged relative to one another the configurational entropy of the chain elements remains unaltered[126]. The total entropy of the system will, however, be raised by the amount $R\rho$, ρ being the fraction of units crosslinked. If the heat and entropy of fusion of the crystallizing units are unaffected by the crosslinks then it is found that

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)\rho \tag{26}$$

where T_m is the melting temperature of the network. This equation is the limiting form of Equation (23) which describes the melting temperature of random copolymers. Utilizing the values of ΔH_u determined for natural rubber and polyethylene, Equation (26) predicts that at most a 2° to 3° depression of the melting temperature should be observed for the networks studied. This conclusion is clearly not in accord with the experimental observation.

The basic assumption has been made in deriving this equation that equilibrium conditions prevail so that the development of crystallinity in the chain direction is impeded solely by the occurrence of the noncrystallizing crosslinked units and the lateral development of crystallinity is essentially unrestricted. If these equilibrium crystallization conditions are not fulfilled then Equation (26) will not be applicable, and a more severe melting point depression would be expected. Wide angle x-ray diffraction studies for both polyethylene and natural rubber networks show in fact that a progressive broadening of the reflections from the different crystalline planes occurs with increased amounts of crosslinking. These observations can be interpreted as being due either to decreasing crystallite size, to the development of further imperfections in the crystallites, or can be attributed to strain. Irrespective of which of these effects is the cause of the x-ray diffraction line broadening they each will contribute to a depression of the melting point. It can be concluded, therefore, that a major contribution to the depression of the melting point of polymer networks is the fact that the perfection of the crystallinity that can be developed, even after careful annealing procedures, is severely restricted due to the crosslinks. Permanent types of crosslinks can be expected to impede the lateral accretion of polymer chains which is necessary in order to form the larger crystallites. Since the crosslinks under consideration are tetrafunctional, nearest neighbor units may also be prevented from crystallizing. Therefore, longitudinal development will be restricted to a greater extent than would be expected solely from consideration of the number of crosslinks.

The networks considered above have been those which were formed when the constitutent polymer chains were in the randomly coiled configuration. Networks have recently been prepared from natural rubber where at the time of network formation the chains were in a highly oriented or fibrous state[127]. This can be accomplished by subjecting fibrous natural rubber, racked according to the procedures of Feuchter[131], to the action of ionizing radiation. The melting temperatures of networks of this type, determined after retraction, recrystallization merely by cooling, and subsequent fusion, differ considerably from those of comparable networks formed by the same procedure from random chains[129]. This is illustrated in Figure 11 where the dependence of the melting temperature on the fraction of units crosslinked, ρ, is given for the two extreme types of natural rubber networks. The lower curve represents the results for networks formed when the chains are randomly coiled. The depression of the

melting point with crosslinking density in this instance is very similar to the results given in Figure 10 for chemically crosslinked networks. The upper curve represents the new situation where the chains were in a highly oriented state during crosslinking. For these networks only a very slight depression of T_m is observed over an appreciable crosslinking range. At any crosslinking level, T_m is greater for networks of this type than for those formed from random chains, the difference in melting temperature between the two network types becoming greater as the crosslinking level is increased.

The basis for the difference in melting temperature for these two different network types finds explanation in the theoretical considerations of Flory[126]. When axially oriented chains are crosslinked it is required that the two units crosslinked must be in adjacent positions on neighboring molecules, this position being predetermined by the orientation process. Though crosslinks may be randomly distributed throughout the specimen the crosslinking process itself

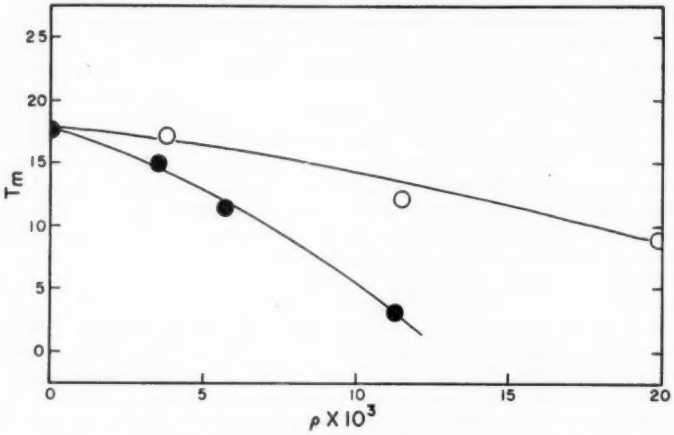

FIG. 11.—Plot of isotropic melting temperature of natural rubber networks formed by irradiation. Chains random, ●; chains oriented, ○. Reference 129.

does not involve the random selection of pairs of units. An ordering is therefore imposed on the system which will persist in the liquid state due to the permanent nature of the crosslinks. This ordering process will result in a decrease in the configurational entropy in the liquid state and consequently in the entropy of fusion. Thus, insofar as the introduction of crosslinks does not alter the heat of fusion of the system, networks formed from ordered chains should possess melting temperatures greater than that of the noncrosslinked system from which it was formed.

Flory has calculated that for networks formed by crosslinking polymer chains held in parallel array, where the aforementioned conditions are fulfilled, the isotropic melting temperature (which is to be distinguished from the shrinkage temperature), determined in the manner described, should increase with the fraction of units crosslinked. More quantitatively

$$1/T_m^0 - 1/T_m^i = (R\nu/N_s\Delta h_u)(A - 3/4 \ln \nu/N_s) \qquad (27)$$

where T_m^i is the melting point of a network composed of ν chains, N_s is the total number of statistical elements in the system, Δh_u the heat of fusion per mole of statistical elements, and A is a constant. A similar equation can be developed from an expression for the entropy of fusion given by Schellman[54]. Equation (27) can be approximated by

$$1/T_m^0 - 1/T_m^i = (R\rho/\Delta H_u)(9/4 - 3/4 \ln (\rho k)) \quad (28)$$

where k is the number of chemical repeating units which can be identified with a statistical element. In this approximation it can be deduced that for natural rubber networks formed from perfectly axially ordered chains, the melting temperature should increase by about 8° for ρ equal to 1×10^{-2} if two isoprene units are identified with a statistical element.

For certain of the fibrous proteins such as collagen and keratin where it can be reasonably assumed that crystallization of crosslinked units is not impeded, an increase in the melting temperature with crosslinking is in fact observed[132, 133]. The networks formed from fibrous natural rubber, however, show a slight decrease in melting temperature with crosslinking. This observation can again be attributed to the effect of the crosslinks in preventing the development of as perfect crystallinity as is developed in noncrosslinked systems. For synthetic polymers it is therefore more reasonable to compare, by means of Equation (28), the difference in melting temperatures of the two types of networks. The assumption is therefore made that the depression of the melting temperature due to imperfections is the same in both cases. T_m^0 is then identified with the melting temperature of the network formed from random chains and T_m^i with the corresponding temperature for networks formed from ordered chains. When this procedure is adopted, good agreement is obtained between the experimental data of Figure 11 and Equation (28) when values of k ranging from 1 to 3 are utilized[129].

It can be concluded from these results that the crosslinking of axially ordered chains imparts an order to the system which is maintained in the amorphous or isotropic state. A partially ordered liquid is developed so that the entropy of fusion is decreased, with the result that the melting temperature is substantially greater than a comparable network formed from random chains. The question then arises as to the kind of order a system must possess prior to crosslinking for this effect to be observed. It has recently been shown[128] that when highly crystalline, but nonoriented, linear polyethylene is crosslinked the isotropic melting temperatures of these networks are appreciably greater than those formed from random polyethylene chains. For networks of the latter type, as is illustrated in Figure 10, a continuous decrease in T_m is observed with crosslinking. On the other hand, for the networks formed from the crystalline polymer, a decrease of only 6.5° is observed in the melting temperature, which remains essentially independent of the number of units crosslinked. The higher T_m observed for networks formed from the crystalline chains is explicable on the same basis as that given for networks formed from fibrous natural rubber. For the crystalline polymer, though the crystallites are randomly arranged relative to one another, portions of the polymer chains are still constrained to lie in parallel array. Since the polymer is predominantly in the crystalline state the crosslinking process again does not involve the random selection of pairs of units. The units which can be paired are limited by the order imposed on the system by crystallization. It is, therefore, not necessary that orientation on a macroscopic scale be present to permit the development of order in the

liquid state. The fact that molecular order is maintained in the liquid state, after crosslinking in the crystalline state, is further substantiated by direct microscopic observation of the polymer melt. It has been found in the case of polyethylene irradiated in the crystalline state that birefringence in a spherulitic pattern persists at temperatures above the melting temperature, while for polyethylene crosslinked while molten no birefringence is observed at corresponding temperatures[128, 134]. Not only are the melting temperatures of networks dependent on the chain arrangement prior to crosslinking but many other network properties which depend on the configurational entropy in the liquid state will be similarly affected[127, 135].

Despite the fact that the melting temperatures of networks formed from ordered chains are substantially greater than those of corresponding networks formed from random chains containing the same number of crosslinks, no network of a synthetic polymer has as yet been prepared in which the isotropic melting temperature in the undiluted state is greater than that of the noncrosslinked system from which it is formed. This is not the case, however, when fusion occurs while the network is in contact with a large excess of diluent. Upon melting, the networks in the amorphous state will imbibe large quantities of the surrounding fluid; the amount of swelling that occurs will depend primarily on the fraction of units crosslinked, the temperature, and the polymer-diluent thermodynamic interaction parameter. Conversely, on crystallization, diluent is exuded from the system.

The equilibrium melting temperature for this experiment represents the situation where three phases coexist in equilibrium. One phase consisting of one component is the crystalline phase. It is in equilibrium with the two-component amorphous network-diluent phase and the one-component supernatant phase. The equilibrium between the latter two phases requires the maintenance of swelling equilibrium so that the composition of the mixed phase is specified. The equilibrium conditions between the crystalline phase and the mixed phase result in an expression similar to Equation (5), with the composition fixed.

It has been reported[128] that for polyethylene networks immersed in an excess of xylene the depression of the melting temperature relative to that of the undiluted network follows Equation (5) when v_1 is identified with the volume fraction of diluent imbibed after melting. This is true both for networks formed from random polyethylene chains as well as for networks formed when the polymer is in the crystalline state. When immersed in xylene, the networks formed in the crystalline state display a significant increase of melting temperature with crosslinking, while for networks formed from random chains a slight decrease is observed. This situation occurs because T_m of the undiluted networks decreases with crosslinking at different rates while the effect of diluent is essentially the same in both cases. These results are to be contrasted with the melting temperature of undiluted networks previously discussed, where regardless of the chain disposition prior to network formation a decrease in T_m is invariably observed.

The increase of the melting temperature with crossslinking density of the networks formed from ordered chains while immersed in an excess of diluent is the first example of this effect with the more flexible chain type molecules and is reminiscent of similar observations for the fibrous proteins. According to theory[126] when ordered chains are crosslinked a continuous increase of the melting temperature with crosslinking density is expected. This is in fact observed with certain of the fibrous proteins[132, 133]. However, the melting of

the fibrous proteins is invariably observed when the polymers are immersed in a suitable liquid medium. The change in swelling equilibrium in the liquid phase that will occur as a result of the change in crosslinking density will also affect the melting temperature. Thus as crosslinking increases, swelling in the liquid still will decrease, and an increase in T_m will be expected from this cause alone. This contribution to the melting temperature could be of the same order as that involved in altering the entropy of fusion by crosslinking oriented chains.

VI. ORIENTATION AND DEFORMATION

One of the unique properties of polymer molecules is the ability to withstand large deformations in the liquid state. It is possible, therefore, for a deformed polymeric system, under appropriate conditions, to crystallize in such a manner that the crystalline regions are preferentially oriented along a fixed direction in space. This is in contrast to the case where crystallinity is induced in the absence of deformation, wherein the crystallites formed are randomly arranged relative to one another. For the oriented system, the crystal-to-liquid transformation will still occur at a given temperature, with the usual changes in physical and thermodynamic properties taking place. However, though fusion is occurring it must be carefully ascertained whether conditions are such that the transformation can be considered a reversible process. This precaution must be taken since in polymer systems it is possible for the orientation to be imposed in the crystalline state without the required equilibrium forces being maintained. If these conditions prevail, then upon crystallization subsequent to the initial melting the original oriented state will not be regenerated.

The possible nonequilibrium aspects of the melting of an oriented polymer system was discussed in connection with the melting of "stark" rubber[136]. When natural rubber is stored in temperate climates it is frequently found to become hard and inelastic because of the development of significant amounts of crystallinity. Upon initial heating, the melting points are found to be significantly higher than that assigned to the equilibrium melting temperature of natural rubber (in the absence of any external force). This apparent contradiction can be readily resolved, since it can be shown that for stark rubber, despite the absence of any external force the crystalline regions are in fact oriented[136]. The maintenance of this orientation during fusion must necessarily result in an elevated melting temperature. The plantation processing of the natural rubber has therefore resulted in the development of oriented crystallization. After the initial melting and subsequent crystallization, melting points which are normal for natural rubber are observed since oriented crystallization does not develop.

Many polymers can be rendered fibrous, i.e. possessing high axial orientation of the crystallites by suitable mechanical means. This condition can be easily maintained below the melting temperature without any external force being applied. On melting, in addition to the usual changes in properties that take place, a large axial contraction is observed. The temperature of this transformation has therefore been designated as the shrinkage temperature. It is found that only under certain conditions (see Section VII) can this temperature be identified with the equilibrium melting temperature. In general the original state is not regenerated merely by reversing the melting process. Thus the application of thermodynamic methods to study the effect of diluent[45] or the effect of tensile forces[137] on the shrinkage temperature would not in general be a valid procedure.

Despite the fact that irreversible melting is a commonly observed feature of oriented crystalline polymers, the possibilities of conducting the transformation in such systems under equilibrium conditions should not be disregarded. In fact the treatment of this problem from the point of view of phase equilibria leads to certain general relations between crystallization, deformation, and dimensional changes[126, 138].

For simplicity we limit consideration to the type of deformation wherein a unidirectional tensile force is imposed on an amorphous network, the polymer being crosslinked so that the deformation process can be carried out in a reversible manner. When sufficiently elongated and held at fixed length, crystallization will ensue. X-ray diffraction studies indicate that almost universally the chain direction within the crystallites will be preferentially directed along the axis of deformation for isothermal crystallization conditions. The equilibrium existing between the axially oriented crystalline phase and the coexisting amorphous phase, subject to the tensile force f, is now considered. It is shown[126, 138, 139] that

$$(\partial f/\partial T)_{P,eq} = -\Delta S/\Delta L \tag{29}$$

where ΔS and ΔL are the changes in entropy and length that occur on fusion of the entire fiber under the conditions specified by f, T, and P. The subscript eq indicates that equilibrium conditions prevail throughout the system. The change in entropy that occurs on melting can be expressed as

$$\Delta S = (\Delta H - f\Delta L)/T \tag{30}$$

where ΔH is the enthalpy change. Equations (29) and (30) can be combined to yield

$$[\partial(f/T)/\partial(1/T)]_p = \Delta H/\Delta L \tag{31}$$

Equations (29) and (31) are the variations of the Clausius-Clapeyron equation which are applicable to the two phase equilibrium between the oriented crystalline and amorphous regions of a polymer network. The striking analogy between this equilibrium and the vapor-liquid equilibrium, or the solid-liquid equilibrium of monomeric substances, becomes apparent when it is realized that in Equations (29) and (31), $-f$ and L correspond to the pressure and volume in the more conventional usage of the Clausius-Clapeyron equation. At the temperature of vapor-liquid equilibrium for a one component system the pressure is independent of the volume of the system, i.e. independent of the relative abundance of each phase. In a similar manner it is expected that under analogous conditions the equilibrium force should be independent of the length of the network until the transformation is complete.

Experimental results reported by Oth and Flory[140] concerned with equilibrium studies of the force-length-temperature relations of crosslinked fibrous natural rubber give strong support to the concept that this phenomenon can be treated as a classical problem in phase equilibria. Their basic experiments involved determining the force f_{eq} that is required to maintain the equilibrium between the two coexisting phases at various temperatures above the isotropic melting temperature of the network. These rather intricate experiments were carried out by initiating the transformation at a temperature above the shrinkage temperature and then preventing its completion by either increasing the force, lowering the temperature, or doing both. Equilibrium can be approached

from several directions in these experiments and f_{eq} thus established. It is found that as long as the two phases coexist f_{eq} is independent of the length of the specimen, as is required by theory. In Figure 12 there is a plot of the variation of the equilibrium force as a function of temperature for a given network. When these data are extrapolated to zero force the isotropic melting temperature $T_m{}^i$ is obtained. In this case it is found to be 6° below the measured shrinkage temperature. The shrinkage temperature in reality represents the amount of superheating that is necessary to induce the transformation. The required equilibrium force f_{eq} continuously increases with increasing temperature, and based on the cross section of the fiber, stresses of the order of 3–4 kg/cm^2 are required to maintain the equilibrium. The stresses required to maintain the equilibrium, i.e., prevent complete melting at temperatures above $T_m{}^i$, are thus quite substantial and could be further increased by elevating the temperature.

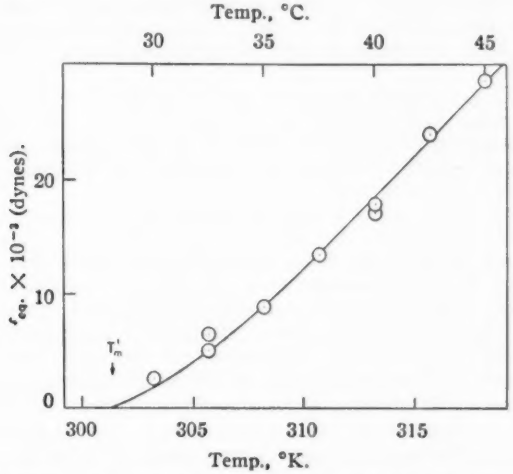

FIG. 12.—Force required for phase equilibrium plotted against the absolute temperature for fibrous natural rubber. $\rho = 1.56 \times 10^{-3}$ and $T_m{}^i = 302°$ K. Oth and Flory[140].

Just as in the study of monomeric substances an analysis of the variation of the transformation temperature with pressure can yield the latent heat of vaporization or of fusion by invoking the Clapeyron equation, so can the variation of transformation temperature with force in the experiments of Oth and Flory[140] be analyzed by means of Equation (31) to yield the heat of fusion involved in the transformation. When cognizance is taken of the fact that initially the fiber is not completely crystalline, the heat of fusion per chain repeating unit ΔH_u can be calculated from these data. It is found from the data for three different natural rubber networks that $\Delta H_u = 1280 \pm 150$ cal/mole of isoprene units. This result stands in good agreement with the value of 1040 ± 60 cal/mole previously determined for this quantity from studies of the depression of the melting temperature by diluents. One can then conclude that in the two-phase region the dependence of the equilibrium stress on temperature follows the dictates of thermodynamic theory.

The experiments just described were carried out on the undiluted polymer since, for fibrous natural rubber, equilibrium can be established at the required temperatures without any degradation occurring. However, for many oriented systems, including the fibrous proteins, similar types of experiments can only be carried out in the presence of appropriate diluents. For the analyses of these latter type experiments Equation (31) must be revised. When the fiber is immersed in an excess of diluent it is required that besides the equilibrium between the crystalline and amorphous regions of the fiber the chemical potential of the diluent in the amorphous phase must be equal to the chemical potential of the diluent in the supernatant phase. It is assumed that the diluent is present only in the amorphous phase. The assumption that the crystalline phase is unaffected by the presence of diluent appears to be well justified in the case of the synthetic polymers, but may have to be modified for certain of the fibrous proteins in selected media. Since the two-component amorphous phase is in equilibrium with two pure phases, the equilibrium force will be determined solely by the temperature if the pressure is maintained constant. The appropriate equation expressing the equilibrium condition can be written as[126]

$$[\partial(f/T)/\partial(1/T)]_{p,L} = \overline{\overline{\Delta H}}/\overline{\overline{\Delta L}} \tag{32}$$

where $\overline{\overline{\Delta H}}$ and $\overline{\overline{\Delta L}}$ represent the sum of the latent changes that occur on melting and the integral changes for mixing with solvent to the equilibrium concentration of the two-component phase.

Experiments similar to those described for fibrous natural rubber have been reported for fibrous crosslinked collagen, the polymer being obtained from rat tail tendon. However, these fibers are maintained in a large excess of $3M$ KCNS solution during the course of the experiments[141]. It was found that the force necessary to maintain equilibrium was again independent of the length of the fiber, as long as a crystalline portion remained in equilibrium. Furthermore, the spontaneous shrinkage temperature (at zero force) was found to be appreciably greater than the equilibrium melting temperature. From an analysis of the relation between the experimentally observed equilibrium force as a function of temperature, $\overline{\overline{\Delta H}}$ was determined. The contribution of the heat of dilution to this quantity was estimated from the temperature coefficient of the equilibrium swelling in the amorphous state. The heat of dilution is negative for the system under study and makes an appreciable contribution to $\overline{\overline{\Delta H}}$. From these experiments ΔH_u can be assigned a value from 1200–1500 cal/mole of peptide units, which is in good agreement with the value determined by other methods for this fibrous protein[14]. It should be emphasized that the application of Equation (31) or (32) to experiments where the spontaneous shrinkage temperature is measured as a function of the applied tensile force is invalid and will lead to erroneous conclusions in regard to the values of the thermodynamic quantities involved in fusion[45, 137].

Another case that can be considered is one wherein the fibrous polymer is in contact with a fixed amount of diluent; i.e., one is dealing with a closed system. For this situation[126]

$$[\partial(f/T)/\partial(1/T)]_{p,\lambda} = \overline{\overline{\Delta H}}/\overline{\overline{\Delta L}} \tag{33}$$

where $\overline{\overline{\Delta H}}$ and $\overline{\overline{\Delta L}}$ now represent the sum of the latent changes and the differential changes that occur on mixing with diluent. These quantities will de-

pend on the composition of the amorphous phase, which in turn will depend on $1 - \lambda$, the fraction of the fiber crystalline. Consequently, in contrast to the other cases considered, the equilibrium force will depend on the amount transformed and hence on the length of the specimen. Suitable experiments by which to assess the validity of the conclusions drawn from Equation (33) have not as yet been reported.

Equation (31) can also be integrated between specified limits, and relations between f_{eq} and the melting temperature are obtained if equations relating f_{eq} to the length are furnished. This is analogous to integrating the Clausius-Clapeyron equation for liquid-vapor equilibrium. The dependence of the pressure on temperature in this instance being obtained only if the equation of state relating the pressure to the volume is given.

For deformed polymer networks the relation between the force to the length is obtained from the statistical theory of rubber elasticity[126]. For a one-component network it can be expressed as

$$f = 3kT\nu(L_a/L_m^2)(1 - L_i^3/L_a^3) \tag{34}$$

where L_i is the isotropic length of the network, the length under zero force, L_a is the length in the amorphous state under the equilibrium tensile force f, and L_m is the length of the sample at maximum extension. For large deformations, where $L_a \gg L_i$, Equation (34) can be written as

$$f \cong k\nu T\, n'\, L_a/L_m^2 \tag{35}$$

where n' is the number of statistical elements in the equivalent freely rotating chain[142]. Substituting Equation (34) into Equation (31), recalling that $\Delta L = L_c - L_a$ and assuming L_c is a constant, there is obtained upon integrating between the limits L_i and L_a and the limits T_m and $T_m{}^i$ the expression

$$2[L_a - L_c][L_a - L_i^3/L_a^2] - [(L_a^2 + 2L_i^3)/(L_a - 3L_i^2)] = 2L_m^2(\Delta h'/3R)(1/T_m - 1/T_m{}^i) \tag{36}$$

If the deformation is sufficiently large so that Equation (35) can be employed, the corresponding expression

$$(L_a^2 - 2L_aL_c)/L_m^2 = (2\Delta h'/3R)(1/T_m - 1/T_m{}^i) \tag{37}$$

is obtained. Equations (36) and (37) express the dependence of the melting temperature T_m of a network on the deformed length L_a in the amorphous state, $T_m{}^i$ being the melting temperature of the network at zero force. It can be readily seen from these equations that the melting temperature must increase with deformation.

The relation between the equilibrium force and the melting temperature can be expressed, in the approximation of large extension, as

$$(f/T)_{eq} = [3k\, n'/L_m][(L_c/L_m) \pm \sqrt{(L_c/L_m)^2 + (2\Delta h'/3R)(1/T_m - 1/T_m{}^i)}] \tag{38}$$

Instead of using L_i and $T_m{}^i$ as a set of limits for the integration, one can alternatively select L_c the crystalline length and $T_m{}^c$ the melting temperature

under a tensile force such that $L_a = L_c$. Corresponding to Equations (36), (37), and (38) there are obtained

$$[(L_c - L_a)/L_m]^2[1 + 2L_i^3/L_cL_a^2] = (2\Delta h'/3R)(1/T_m - 1/T_m^c) \quad (39)$$

$$(L_c - L_a)^2/L_m^2 = (2\Delta h'/3R)(1/T_m - 1/T_m^c \quad (40)$$

$$(f/T)_{eq} = (3k\,n'/L_m)(L_c/L_m \pm \sqrt{(2\Delta h'/3R)(1/T_m - 1/T_m^c)} \quad (41)$$

At temperatures such that $T_m < T_m^c$ two solutions are obtained for L_a, one being less than and the other greater than L_c. Since most polymer chains will suffer rupture at length in the amorphous state approaching maximum extension the physical reality of the second of the two solutions for L_a is somewhat tenuous. It can also be shown from Equation (39) that no real solutions exist for L_a at temperatures greater than T_m^c. Thus T_m^c assumes the role of a critical temperature, since above this temperature the crystalline phase cannot exist. This temperature is analogous to the critical temperature for liquid-vapor equilibrium of monomeric materials, being a temperature above which the liquid phase cannot exist regardless of the applied pressure.

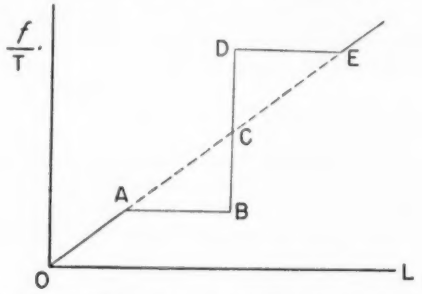

FIG. 13.—Plot of f/T against length L for polymer networks undergoing crystal-liquid transformation, Flory[126].

A physical interpretation of the significance of Equations (36–41) can be given by resorting to a graphical representation as in Figure 13[126]. If the deformation process is initiated at a temperature such that the network is in the amorphous state and if Equation (35) represents the equation of state, f/T will increase linearly with L until crystallization sets in. This is represented by point A in the figure. This point represents the melting temperature of the network under the specified force and elongation. As crystallinity develops, the length of the specimen will increase along the line AB. For the one-component system being considered the force must remain invariant until the transformation is complete at point B. It is the lesser of the two roots of Equation (38) or (41) which is applicable to this equilibrium. The stress is then assumed to rise almost vertically with only slight elongation in the highly rigid crystalline state that is developed at B.

If it is allowed that a state where $L_a > L_c$ can actually be attained then the amorphous phase will be reconstituted along the line DE, with the equilibrium force corresponding to the larger of the two roots of Equations (38) or (41). With increasing temperature the points A and E are displaced towards C, and a

temperature is reached where the equilibrium lines AB and DE vanish. This temperature corresponds to T_m^c, the critical temperature above which crystallization cannot occur. The regeneration of the amorphous phase along the line DE seems hardly a physically realizable situation (due to excessive deformation that is required in the amorphous state) and attention should be focussed principally along the path OABD for real systems. The force-temperature-length relations, as expressed by Equations (36) to (41) and illustrated in Figure 13, are quite general in concept. They do not depend on any detailed crystallographic structure of the crystalline phase as has been often thought. For crystallizable networks immersed in diluents a similar type analysis can be made by utilizing Equation (32) or (33) and the appropriate equations of state.

The experimental results reported by Oth and Flory[140] from their study of two-phase equilibria of fibrous natural rubber lend themselves to the graphical presentation of the ideas outline above. A compilation of these data is given in Figure 14 where the equilibrium force as a function of the length of the specimen is plotted at the various indicated temperatures above the isotropic melting temperature. This latter temperature is 302° K for the particular network studied. The horizontal solid lines represent the stresses necessary to maintain the two phases in equilibrium. As has been previously indicated, it is independent of sample length. The length of the specimen, upon the completion of the melting, at the given force and temperature, is indicated by the solid circles. The dashed lines represent the dependence of the force on length at each temperature in the amorphous state as calculated by means of Equation (34). The force-length relation in the crystalline state at 303.2° K is indicated by the vertically rising straight lines. The corresponding isotherms in this state for other temperatures would be expected to be similar in nature. The set of isotherms plotted in this figure which encompass the crystalline and liquid phases correspond to the isotherms in a p-v diagram describing vapor-liquid condensation.

In Figure 14 the increase in the melting temperature that occurs with extension or applied force is readily discerned. Illustrated most vividly in this figure, however, are the equilibrium relations that exist between the force, length, and temperature when conditions are varied so that a network traverses the two phase region. Consider, for example, a network maintained under conditions specified by point A in Figure 14. This point corresponds to a network 8 cm. long in phase equilibrium at 303.2° K under a tension slightly less than 4×10^5 dynes/cm^2. If a process is carried out so that the temperature is increased, while it is required that the length be maintained constant, a path described by a vertical line upward from point A will be followed. In order for the length to be maintained constant, the isotherms of Figure 14 show that external force must be applied to balance the retractive force developed by the crystalline network. The additional stress must be applied to prevent melting as the temperature is increased. If melting occurs the original dimensions will not be preserved and the length of the sample will diminish considerably. If the temperature is raised to 318.2° K and the length maintained constant, a tension of 4 kg/cm^2 is developed. This tension is of the same order of magnitude as that developed by the muscle fiber system in tetanic contraction. For the fibrous natural rubber networks still greater tension could be developed by merely increasing the temperature. The stress will continuously increase with temperature as long as the two-phase region is maintained; i.e., until the critical temperature T^c_m is reached. A fundamental mechanism is thus available by which large tensions can be developed in axially oriented crystalline macromolecular

systems. Though the data that are available and illustrated are for fibrous natural rubber, this mechanism is an inherent property of axially oriented crystalline polymers and should find applicability irrespective of the chemical nature of the polymer chains and the methods by which melting is induced. Recourse to the diagram in Figure 14 indicates clearly that the increase in stress that can be developed with increasing temperature by the aforementioned process is much greater than can be developed by increasing the temperature of an amorphous network maintained at constant length.

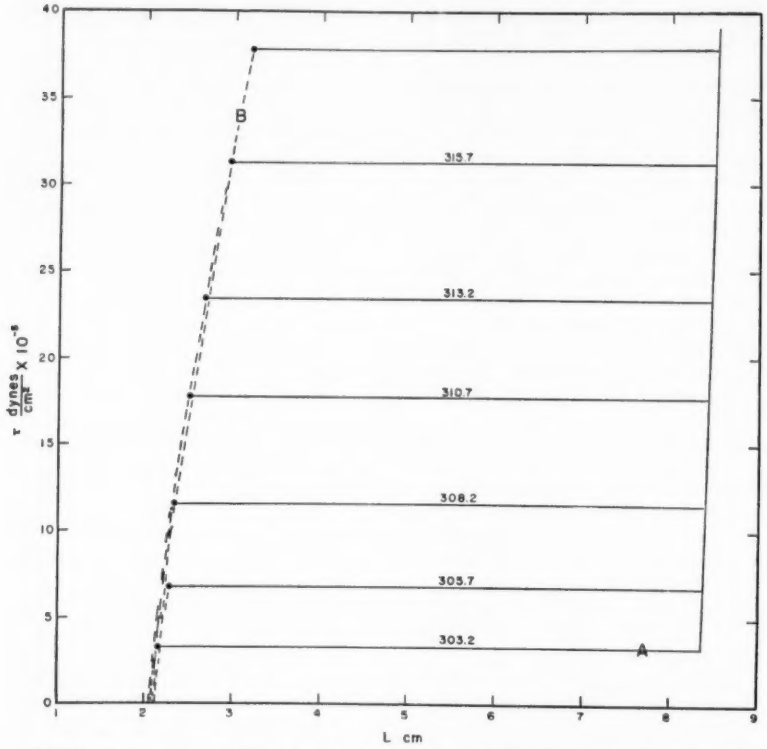

FIG. 14.—Composite plot of tension-length relation at various temperatures for fibrous natural rubber. Dashed line for amorphous state calculated from Equation (34). Data from Oth and Flory[146]. (Note: The number 318.2 for the topmost plot has been omitted in the figure.)

One can also consider the inverse process, by starting with a network in the amorphous state, as is illustrated by point B of the figure. At 318.2° K the network is in the amorphous state and has a length of 3 cm under a stress of 34×10^5 dynes/cm². If the temperature is now lowered, while the requirement that the length be constant is again maintained, a path vertically downward from point B will be followed. Oriented crystallinity will develop as the temperature is lowered and the two-phase region is entered. As is indicated in the diagram the equilibrium stress will concomitantly decrease. At 303.2° K the

stress will have decreased about 10 fold. Thus a formal basis is provided for the explanation of the experimental results of Smith and Saylor[143], Tobolsky and Brown[144], and Gent[145] where a relaxation of the stress is observed during the oriented crystallization of natural rubber networks held at fixed length. The molecular basis for this decay in stress resides in rubber elasticity theory[138]. According to theory, the retractive force exerted on the ends of a chain maintained at fixed length is proportional to the number of statistical elements contained in the chain and the magnitude of the end-to-end distance. During crystallization both these quantities are reduced. The number of statistical elements will be decreased by the number of units crystallizing. The distance traversed by a collection of chain units in the crystalline state greatly exceeds the corresponding distance in the amorphous state. Therefore, the distance between fixed crosslinks encompassed by the remaining noncrystalline units will also be reduced. For these reasons, therefore, the stress must decay.

It has recently been reported[146] that for vulcanized silica-filled polydimethylsiloxane the tension increases during crystallization at fixed length. This apparent contradiction could be resolved if a significant proportion of the crystallites did not develop with the chain direction preferentially directed along the macroscopic fiber axis. This possibility is supported by the wide angle x-ray diffraction studies for this system[147].

Processes can also occur where the stress rather than the length is maintained constant as the temperature is varied. Consider our system (in the crystalline state) once again at point A in Figure 14. If the stress in now maintained constant while the temperature is raised, a horizontal path will be followed which will terminate at the appropriate dashed curve representing the amorphous state. Accompanying the transformation a four-fold diminution in length will be observed. This process is reversible as long as the equilibrium stress is maintained. If the temperature is therefore lowered so that the original temperature is regained, a spontaneous elongation will accompany the transformation from the amorphous to the crystalline state. Shrinkage accompanying the melting of axially oriented polymers has been widely observed. A spontaneous increase in length during the crystallization of deformed natural rubber networks held at constant force has been reported by Smith and Saylor[143].

The melting-crystallization cycle of a network in which an equilibrium is maintained results in a reversible contractile system. Thus a fundamental mechanism is available to macromolecular systems by which large anisotropic changes in dimensions can be incurred. Since the dimensional changes occur as a result of a phase transformation they are observed over a very narrow temperature range. If the network is composed of a copolymer (not all of whose units participate in the crystallization), the same phenomenon will be observed on melting, but since the melting range must by necessity be broadened, the axial contraction will occur over a wider temperature interval. For networks immersed in diluents the same principles also apply but the changes in swelling that occur will affect the magnitude of the dimensional changes.

Because of the two states in which a polymer network can exist certain unique thermoelastic coefficients are observed[138]. For an ideal network in the liquid state the retractive force can be attributed solely to entropy effects. Thus at fixed length the force will increase directly with the absolute temperature, while at fixed force the length will decrease with the reciprocal of the absolute temperature so that a negative thermal expansion coefficient is observed. However, for a crystalline network where the degree of crystallinity does not change with temperature a normal positive thermal expansion co-

efficient will be observed. If the degree of crystallinity varies with temperature, then if the length is held constant while the temperature is raised, the force will increase. While held at constant force the length will diminish with temperature as partial melting occurs.

In summary there are two very important generalizations which result from consideration of the crystal-liquid transformation of oriented polymer networks. One is the fact that large tensions are developed when the fusion is carried out at fixed length. Alternatively, a large diminution in axial dimensions occurs when the process is carried out at constant force. These two phenomena are inherent properties of macromolecular systems which are clearly elucidated when the crystal-liquid transformation is treated as a problem in phase equilibria. These phenomena have not as yet received the complete attention and study commensurate with their prime importance, particularly in describing the behavior of naturally occurring polymer systems. It is doubtful that there is any other mechanism whereby such large forces can be developed or that such large anisotropic dimensional changes can take place in a macromolecular system.

VII. DIMENSIONAL CHANGES

From the discussion in the previous section it is expected that when a polymer crystallizes so that a preferential axial orientation of the crystallites is developed, an increase in length will accompany the transformation. Conversely, upon melting, an axially oriented polymer contraction will occur. In most systems, in order for this process to be carried out reversibly, equilibrium conditions require that a specified tensile force be imposed. Thus, for example, at the isotropic melting temperature of most networks anisotropic dimensional changes are not observed since in the absence of an external force oriented crystallinity has not been developed. On the other hand, it is possible to develop oriented crystallization without an external force being maintained, as for example the case of natural rubber which has been rendered fibrous[127] or in the natural-occurring polymer collagen[61]. As is illustrated in Figure 15, a large axial contraction occurs on melting fibrous natural rubber. This is a result of the large difference that exists in the distance traversed by a collection of chain elements in the crystalline and amorphous states. Thus four- to five-fold contractions are easily observed in polymer systems. The shrinkage accompanying the melting of fibrous natural rubber was first described by Page[148] in 1847. A similar behavior is exhibited by collagen and other fibrous polymers[149] which possess the common structural feature of being crystalline and axially oriented. However, on cooling the fibrous natural rubber after the initial melting, though the crystalline state is regenerated, the dimensions are not regained in the absence of an external force since oriented crystallization does not occur. For systems of this type the dimensional changes are irreversible, and the shrinkage temperature does not represent a temperature of thermodynamic equilibrium.

Recent experimental results[150,151] have shown, however, that for appropriately formed crystallizable networks it is possible to develop a reversible contractile system without the application of any external force. To understand the properties of such networks it is necessary to consider the crosslinking process by which they are formed. When a collection of random chains are crosslinked, the isotropic length L_i remains invariant as additional crosslinks are introduced. In contrast, when a collection of axially oriented chains are crosslinked the isotropic length (measured after relaxation of the network)

progressively increases[135,151–153]. It is theoretically expected[126] that L_i will increase in direct proportion with the square root of the fraction of units crosslinked and will also depend on the initial orientation of the systen. These expectations are fulfilled, and substantial increases in the isotropic length have been observed after the crosslinking of fibrous natural rubber[127,135], collagen[152,153], and fibrous polyethylene[151].

The relative increase in length that is developed in the isotropic state after crosslinking, by means of high energy ionizing irradiation, an axially oriented fibrous polyethylene specimen is illustrated in Figure 16. There is plotted in this figure the ratio of L_i/L_o at 140° C against the square root of the radiation dose. The ordinate in this plot represents the relative increase in length that occurs in the amorphous state upon crosslinking highly axially oriented chains, L_o being the length of the specimen in the amorphous state in the absence of

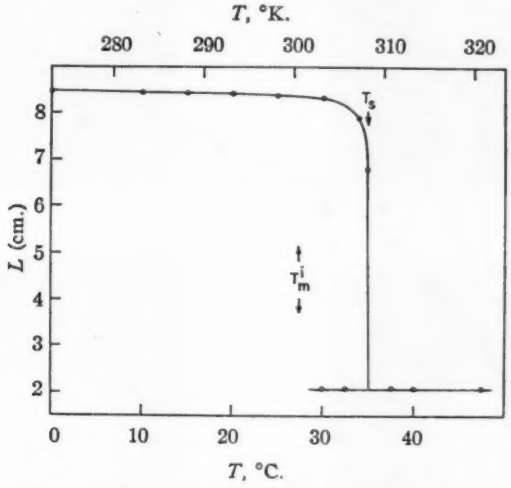

FIG. 15.—Length under zero force, as a function of temperature for fibrous natural rubber, Oth and Flory[140].

crosslinks. It is estimated that for a radiation dose of 1000 megareps approximately 4% of the chain units are crosslinked[151]. The increase in isotropic length that is observed for these networks is quite large; about a twenty-fold extension in the amorphous state is developed by this procedure without the application of any external force. Despite the absence of any imposed tensile force, however, the deformed amorphous network obtained in the manner indicated represents the equilibrium state for the system. There is a very general method available, therefore, which involves the crosslinking of oriented networks, by which large extensions in the amorphous state can be developed without an external force being applied.

The networks described above can be easily crystallized by lowering the temperature. This should be a reversible transformation, since despite the large relative extensions that exist in the amorphous state, it is the equilibrium state. Some typical wide-angle x-ray diffraction patterns characterizing the

recrystallized fibers are given in Figure 17. Crosslinking the initial highly oriented fibers by ionizing radiation results in no significant difference in the wide angle x-ray pattern. However, after crosslinking and following the initial irreversible melting and subsequent recrystallization significant differences are exhibited in the x-ray patterns depending on the number of crosslinks introduced. This can be seen in the figure when patterns for four different samples, representative of different irradiation levels, are given. For the specimen into which no crosslinks have been introduced, the resulting pattern after melting and recrystallization consists of a series of concentric rings. This state is thus characterized by a collection of randomly arranged crystallites. However, it is evident from the other patterns in the figure that as an increasing number of crosslinks are introduced, a preferential orientation of the crystallites progress-

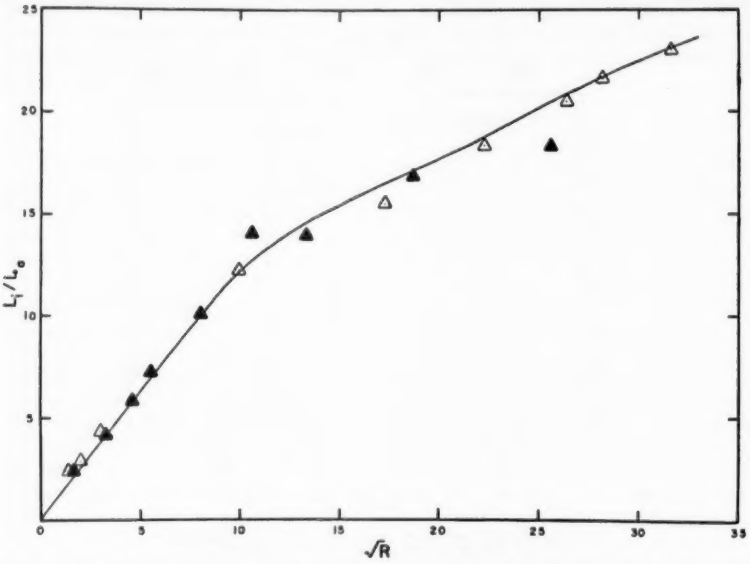

FIG. 16.—Plot of L_i/L_o at 140° C against square root of radiation dose for highly oriented polyethylene fibers. Co^{60} γ-irradiation, ▲; irradiation by high energy electrons, Δ. Reference 152.

ively develops. Thus, the pattern in Figure 17d, which is observed for a fiber which has a value of ρ of approximately 2.65×10^{-2} and L_i/L_o of 18.3, indicates that the c-axes of the crystallites (the chain direction) are again preferentially oriented along the macroscopic fiber axis. Thus a preferential crystallite orientation can be developed by these procedures without maintaining an external stress. This situation must then represent the equilibrium crystalline state of the networks.

The occurrence of this unique situation must be related to the extremely large values of L_i/L_o that are achieved in the amorphous state by the crosslinking process. The large extension ratios that are developed result in the establishment of a preferential axis for recrystallization of the polyethylene specimens. Evidence for the preferential axial recrystallization of networks

formed from fibrous natural rubber has also been given by Oth and Flory[140]. In the polyethylene fibers thus developed, the preferred axial orientation of the crystallites are an inherent part of the system and will be present after any subsequent melting and recrystallization cycles provided that the intermolecular crosslinkages are maintained.

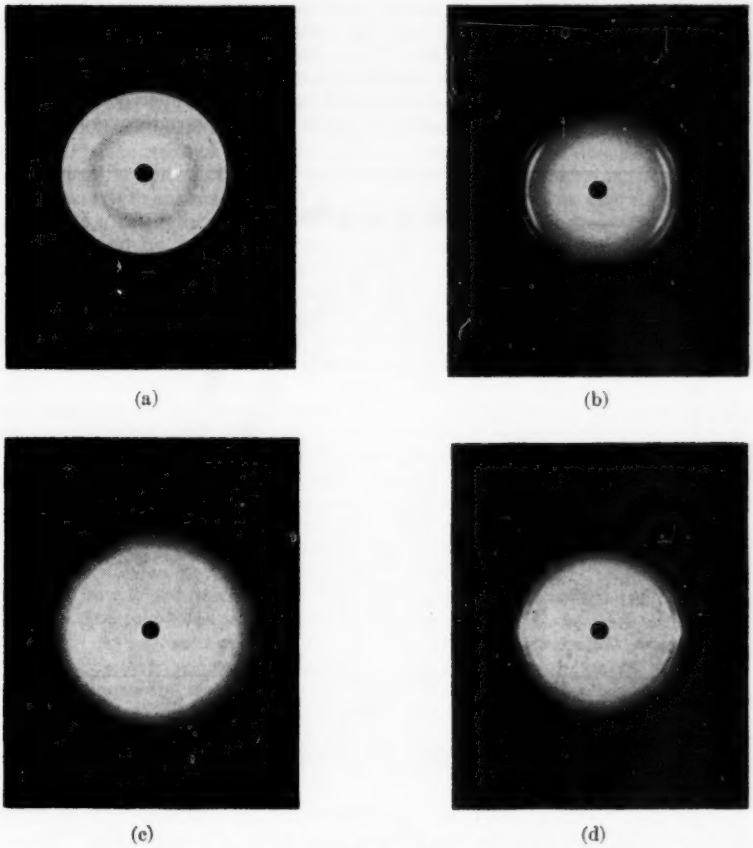

FIG. 17.—Wide-angle x-ray diffraction patterns, taken at room temperature, of crosslinked recrystallized polyethylene fibers for various radiation doses. (a) $R = 0$, $L_i/L_0 = 1$; (b) $R = 179$ megareps, $L_i/L_0 = 13.7$; (c) $R = 353$ megareps, $L_i/L_0 = 16.8$; (d) $R = 660$ megareps, $L_i/L_0 = 18.3$. Reference 152.

In the previous section the relation between anisotropic dimensional changes and the melting-crystallization cycle of oriented systems has been pointed out. Similar considerations should apply to the fibrous polyethylene just described despite the absence of an external force. Since the polyethylene fibers are axially oriented in the crystalline state contraction would be expected on melting and spontaneous reelongation on crystallization. This expectation is ac-

tually fulfilled, as is evidenced by the plot of Figure 18. Starting in the equilibrium crystalline state (after melting the initially crosslinked fiber and recrystallizing), there is plotted in this figure the relative length as a function of temperature for a fiber corresponding to the one illustrated in Figure 17d. A slight positive thermal expansion coefficient, typical of the crystalline state, is observed during the initial heating. Concomitant with melting, a 25% axial contraction is observed over a narrow interval of temperature. Above the melting temperature the thermal expansion coefficient is slightly positive, as is expected in the liquid state. On cooling, recrystallization of the specimen occurs and the fiber regains its original dimensions. When a slow cooling process is utilized after fusion, as is illustrated in the figure, supercooling occurs. Despite this fact the original dimensions of the specimen are recovered. The

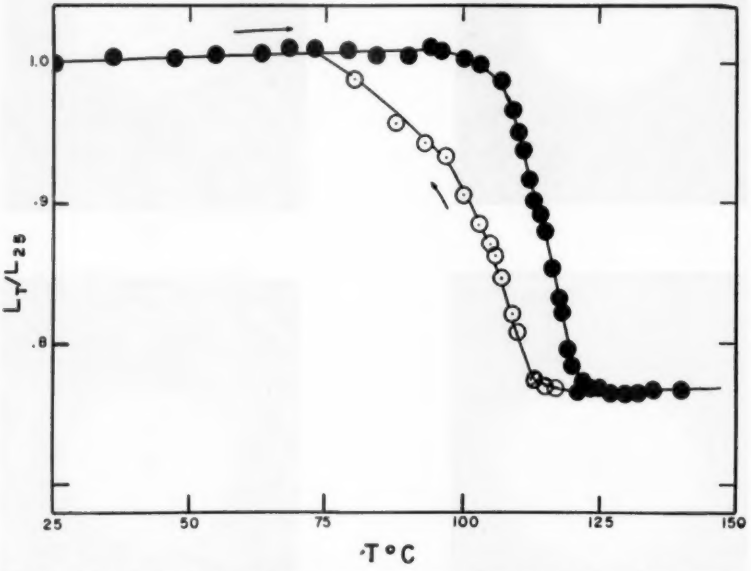

FIG. 18.—Plot of relative length against temperature for reversibly contractile polyethylene fiber. Heating, ● ● ●; cooling, ○ ○ ○. Reference 152.

time required for the return to the crystalline state can be substantially reduced by immediately bringing the sample to a large value of undercooling. Therefore, coupled with the crystal-liquid transformation there is obtained a reversible contractile system which is completely cyclic without the necessity of maintaining any external stress. The shrinkage temperature in this instance can be identified with the equilibrium melting temperature, in contrast to the other cases considered.

The reversible dimensional changes observed result as a consequence of a cooperative phase transformation and will consequently display all the characteristics of such a phenomenon. It has been pointed out by Flory[61,138] and by Pryor[154] that fibers such as described here can serve as the working substance

of an engine that converts thermal energy into mechanical work. The cyclic process described does not require the application of a specified external force but will operate with any applied load consistent with the tensile properties of the fiber. In the polyethylene fiber system described, thermal energy is utilized to initiate the transformation from the crystalline to the amorphous state. This process is, of course, more general and the phase transition can in principle be initiated by an appropriate chemical reaction. Thus for a chemically more reactive fibrous macromolecular system, that is crosslinked in a similar manner to that by which the polyethylene fibers were prepared, reversible anisotropic dimensional changes will still accompany the melting-crystallization cycle. For such a system the transformation could be carried out isothermally utilizing appropriate chemical reactions. If a given reaction induces melting, methods to reverse the reaction must be found in order for recrystallization to occur. Under such conditions the fiber can serve as the working substance of an engine which converts chemical energy to mechanical work. It is, therefore, important that a distinction be made between the actual reversible contractile mechanism caused by melting and recrystallization and that process or chemical reaction which induces the phase transition. When this principle is realized it is then possible to investigate many of the observed and reported contractile systems from a unified point of view. This approach is particularly fruitful in investigating and understanding the anisotropic dimensional changes in various fibrous proteins. For these polymers contractility can be induced by a wide variety of chemical reagents. In addition the reversibility of the dimensional changes observed in macromolecular systems of this type can be understood by taking the crosslinked fibrous polyethylene system as a model.

Various wide angle x-ray diffraction studies have shown that the fibrous proteins occur naturally in the axially oriented crystalline state[10–12]. Therefore an axial contraction is to be expected on melting irrespective of the method by which the melting process is induced. The reversibility of the process will depend on the number of crosslinks imposed on the system and the ability to reverse any chemical reaction which is involved in melting.

It is now well known that when the fibrous protein collagen is heated in water, a five-fold axial contraction occurs at about 70° C, as a consequence of melting. As has been previously indicated, this is an irreversible process since reelongation does not occur on cooling. We can, therefore, conclude that in native collagen the stable type of intermolecular crosslinks required for a preferential axial recrystallization to occur in the absence of an external force is lacking. The amino acid composition of collagen does not provide any basis to expect the presence of such intermolecular crosslinks. It was, however, pointed out by Ewald many years ago[155] that if collagen in the native state is crosslinked (tanned) with formaldehyde, then after hydrothermal shrinkage reelongation will occur on cooling in a reversible manner. Bear[156] has also observed that simultaneously a significant portion of the low angle x-ray diffraction pattern is recovered. Some recent data of Oth[152], demonstrating the reversibility of the dimensional change of collagen fibers crosslinked in the native state by reaction with benzoquinone are given in Figure 19. The initial melting is very sharp, while on cooling, a spontaneous reelongation to about half the original dimension is observed, shrinkage occurring on subsequent melting. This process can then be repeated cyclicly several times. Similar results have been reported for the fibrous protein elastoidin[157,158], in the native state. For this protein, though the amino acid composition is similar to that of collagen, it contains about 1 to 2% cystine residues whose side groups can form intermolecular covalent cross-

links. Thus the role played by intermolecular crosslinks in promoting oriented crystallization from the molten state is similar in both natural and synthetic polymers.

It is well known that the proteins of the keratin class exist in the oriented crystalline state, have a high cystine content and undergo contraction when subject to the action of a wide variety of reagents[159]. It would then be expected in terms of the principles outlined above that if the contraction is a consequence of melting, the process should be reversible if the crosslinkages are maintained. This is found to be the case when the above condition is fulfilled. Thus when either α or β keratin fibers are subjected to conditions conducive to melting, a contraction is observed. If this process occurs without the breaking of intermolecular crosslinks, and the chemical reaction is reversed, crystallization and

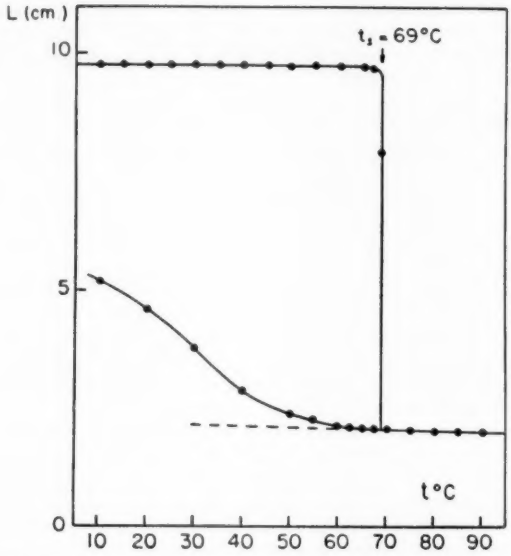

FIG. 19.—Reversible contraction of crosslinked (tanned) collagen fibers. Upper curve, initial melting and shrinkage. Lower curve, melting after recrystallization and spontaneous elongation, Oth[132].

reelongation should occur. This expected behavior can be illustrated by the experimental observations of Whewell and Woods[160,161]. In these experiments, either α or β keratin fibers are immersed in a cuprammonium solution of appropriate concentration and an approximately 20% decrease in length is observed. This shrinkage is accompanied by loss of the characteristic wide angle x-ray diffraction pattern demonstrating that melting accompanies the shrinkage. The melting process in this case appears to be caused by a complexing reaction between amino acid residues and the cuprammonium solution and is carried out isothermally. If the shrunken amorphous fibers are now immersed in dilute acid solution, reversing the chemical reaction, the initial length and x-ray pattern are both regained. This process is again completely analogous to the reversible dimensional changes observed in the polyethylene fibers with the melting

being induced by chemical reaction in this case. It is important to note that if the keratin fibers are immersed in this alkaline medium for too long a time, conditions which are known to be conducive to the severance of disulfide cross-links, although contraction is still observed on melting, the process is no longer reversible.

The examples cited are typical of the dimensional changes observed in the fibrous proteins and represent only a few of the many cases that have been reported or can be observed. It is clear that they are explicable by invoking the same physico-chemical principles applicable to synthetic polymers. For contraction to occur, only very simple requirements need to be fulfilled. Initially there must be present an oriented crystalline state. If the transformation of this state to the amorphous state or under certain conditions to the disoriented crystalline occurs an axial contraction will result. Once it is recognized that melting is the cause of contraction and that there are many ways by which melting can be induced, the fact that contraction can be caused by a variety of reagents is easily understood. The fundamental basis for this mechanism does not find its origin in the detailed crystallographic structure analysis of either of the states. Reversibility of the contraction will depend on the development of axially orienated crystallization from the shrunken state. This, in turn, will depend on an adequate number of intermolecular crosslinks being imposed on the original oriented system and the ability to reverse any chemical reaction causing melting.

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ANALYSIS OF RUBBER *

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INTRODUCTION

In this paper it has been assumed that a completely unknown vulcanized sample is in question for analysis. Although this occurs very rarely in practice it is thought that such an approach would bring out the more important factors in desirable sequence. Thus, although general sources of information are worth first consideration, one might well begin an analysis with identification and determination of elastomers and continue with analyses for sulfur in various forms, accelerators, activators, antioxidants, reinforcers, fillers, etc.

In a later section some attention will be given to analyses of importance as rubber goods are being manufactured; that is, tests on crude rubber and some of the principal compounding materials.

SOURCES OF GENERAL INFORMATION

From a historical, and perhaps a nostalgic point of view, it seems that any paper on the analysis of rubber should mention the book by Tuttle[1], one of the

* Contribution 185 from the Research Center.

earlier American Chemical Society monographs, published in 1922. Of course, this was all based on natural rubber but nevertheless it contains valuable information leading up to analytical methods in use today. Another very valuable book of much later date (1937) is the *Chemistry and Technology of Rubber* edited by Davis and Blake[2]. Only one chapter, the 25th, by Dinsmore, Seeds, and Rutledge is on the analysis of rubber, but a general knowledge of the rest of the book is desirable for any rubber analyst in order that he may use good judgement in applying his procedures. "Davis and Blake" also is essentially based on natural rubber. The need for general information on *synthetic rubber* and its widespread applications in industry, is well served by the more recent book edited by Whitby, Davis, and Dunbrook, under the auspices of the Rubber Division, American Chemical Society, and published in 1954[3]. Wood's chapter, No. 10, entitled the "Physical Chemistry of Synthetic Rubbers" contains much information of an analytical nature.

For detailed methods of analysis of rubber, the best publications available are ASTM Standards[4], Federal Test Method 601[5], and Federal Standard No. 90[6] on Synthetic Rubber and Latex. Probably the ASTM designations of greatest interest are D-297, *Chemical Analysis of Rubber Products;* D-833, *Identification and Quantitative Analysis of Synthetic Elastomers;* D-471, *Changes in Properties of Rubber and Rubber-Like Materials in Liquids;* D-814, *Permeability of Vulcanized Rubber or Synthetic Elastomers to Volatile Liquids;* D1416 *Chemical Analysis of Synthetic Elastomers* (*Solid Butadiene-Styrene Copolymers*); and D1417, *Testing Synthetic Rubber Latices* (*Butadiene-Styrene Copolymers*). Somewhat similar information on cured rubber is contained in British Standard 903[7], *Methods of Testing Vulcanized Rubber.* Unfortunately ASTM and Federal Methods contain very few references to the literature or explanations of theory. British Standard 903 cites a larger number of references, comparatively, but as might be expected is somewhat different from usual American practice. It is well worth consulting when a newer method or application is in question. Two other sources of good information on rubber analysis are the reviews on rubber[8–14] which appear from time to time in *Analytical Chemistry*, and the Bibliographies which come out under the sponsorship of the Rubber Division of the American Chemical Society in book form. The latest of these[15] was recently issued covering the years 1949–51. Sections are included on Latex Analyses, Testing of Rubber—Chemical, and Testing of Rubber—Physical.

At the time that the final draft of this review was being prepared for *Rubber Chemistry and Technology*, the writer obtained a copy of a very recent book on rubber analysis by W. C. Wake[16], of the Research Association of British Rubber Manufacturers. It is a good book. Rapid scanning indicates that Dr. Wake has done well in his stated intention of supplementing the methods of the British Standards Institution and the American Society for Testing Materials.

He cites three comparatively recent books as important in the field of rubber analysis. One is British[17] and therefore in English. The other two are in German[18] and in Russian[19] respectively. Unfortunately the writer is not familiar with any one of the three, but is pleased to have the opportunity to mention them here for completeness.

Dr. Wake seems to have had difficulty with the ASTM or Underwriters' type of extraction apparatus since he criticizes it, in effect, as clumsy and expensive. If suitable holding arrangements are made, the condensers and connecting tubes need not be clumsy in operation. The initial cost is offset by the fact that the condensers should last for years. The quoted number for ASTM

extraction cycles, 110 to 154 in 16 hours, appears to be in error. For the suggested average time of one cycle in three minutes the total for 16 hours should be 320.

In regard to at least one other topic, American readers of Dr. Wake's book may need encouragement. This is the application of the sulfite method for free sulfur. From more than twenty years experience with his own variations, this reviewer believes that a strong case can be presented for the scientific value as well as the practical value of the sulfite method. There is little doubt, however, that more published information is desirable especially in regard to the interference effects of accelerators other than mercaptobenzothiazole (MBT).

IDENTIFICATION AND DETERMINATION OF ELASTOMERS

Perhaps it should be said as a preliminary comment that since the elastomer is normally a major component, the identification or detection of small amounts is not usually required. The determination of an elastomer need only be approximate and might possibly be designated more appropriately as an estimation. Quite often the advice of an experienced compounder is desirable in deciding how much care is needed in a given situation.

The question of reclaim is always a difficult one. The writer knows of no reliable method which can be used to detect or estimate reclaim. Some indication of its presence may perhaps be obtained from higher than usual extracts or physical properties which are a little different from those obtained with unreclaimed elastomers, but at best any conclusion is little more than a guess. A fairly important consideration to the analyst is the fact that the use of reclaim may mean the presence of a small amount of natural rubber in an SBR stock or the reverse. Therefore, in arriving at an overall composition one cannot be too rigid in interpreting analyses for polymers.

IDENTIFICATION

The most complete arrangement of tests for identification purposes is that of Burchfield[20,21]. The first step is pyrolysis in a simple test tube apparatus. Two solutions are used to indicate pH and density of the condensate from the pyrolysis. Color tests with *p*-dimethylaminobenzaldehyde and spot tests with indicator papers add to the information. In favorable cases pyrolysis may even be accomplished by branding the sample with a red hot metal rod. Burchfield's tests have been included in ASTM procedures. However, they require experience and comparison with known samples. As time has gone on since the original publication of these tests the variety of elastomers has increased and the results of the tests have become more difficult to interpret.

Other tests also give useful information. Parker has reported on the reaction time of rubbers in 1:1 mixtures of nitric and sulfuric acids[22] and also on the determination of swelling ratios[23]. Other interesting work of Parker's[24] has been on the identification of Thiokols and on the estimation of polyisobutylene. The Thiokols he distinguishes by their reactions with sodium sulfite, the polyisobutylene he determines by extraction with petroleum ether. Stern[25] has gone into considerable detail in reporting on the analysis of synthetic rubbers and mixtures containing natural rubber.

Although such tests as mentioned above are quite valuable and yield much useful information, it appears to the author that the most suitable procedure or method for use at the present time or in the near future is the application of infrared absorption. A good general discussion with numerous references has

been given by Mann[26]. Much special equipment is required but variations of technique permit applications to almost all types of samples. Qualitative indications are readily obtained but quantative work is much more difficult.

Dinsmore and Smith[27] have written a basic paper on the use of infrared. Following up work on similar lines by Barnes, Williams, Davis and Giesecke[28], they developed a procedure which has since proven quite valuable. In their work with several solvents and a number of elastomers, Dinsmore and Smith found that *o*-dichlorobenzene is the generally most useful solvent and applied it successfully in the analysis of vulcanized samples. In their procedure the solution resulting from the hot digestion of the sample with dichlorobenzene is clarified and concentrated and evaporated on salt plates. The infrared absorption curve is then run in the rock salt region, that is, in the approximate wavelength span of 2 to 16 microns.

The important step to secure solution of an unknown cured sample is an oxidative degradation. For example, the writer has digested two similar portions cut from the same sample, one in a flask under a reflux condenser, the other in a beaker covered with a watch glass and both in boiling *o*-dichlorobenzene on the same hot plate. The sample in the beaker dissolved whereas the one in the flask remained comparatively unaffected in the same heating time. Presumably oxygen from the air had easier access to the sample in the beaker than to the sample in the flask under the condenser.

A valuable contribution to the infrared information and technique has been made by Harms[29]. His paper is under the very general title, *Identification of Complex Organic Materials*, and therefore might easily be overlooked. This is unfortunate because sample absorption curves are given for all of the following materials:

Phenolic resin	Dynel
Urea-formaldehyde resin	Natural rubber
Epoxy resin	Styrene-butadiene rubber
Fluorolube oil	Butyl
Nylon 66	Buna N
Saran	Neoprene
Mylar	Silicone rubber
Dacron	Silicone oil
Terylene	Hycar PA
Orlon	Wire enamels

Harms, like Burchfield, pyrolyzes the sample in a test tube but operates so as to retain the condensate in the cool part of the tube. He then transfers a portion of the condensate to a sodium chloride plate, covers it with a second plate, and determines the infrared absorption of the resulting sandwich in the 2 to 16 micron region.

A recent paper[30] points out that insoluble crosslinked polymers can be analyzed by infrared by the potassium bromide pellet technique. The grinding of the polymer with the potassium bromide requires considerable care. The procedure might conceivably be applied to cured samples but it does not allow for the separation of interfering materials such as carbon black.

This troublesome interference by carbon black in making infrared absorption curves of rubber samples has been reported as overcome by the use of a large aperture reflecting microscope[31]. It is to be hoped that the findings will be confirmed and that such equipment will become readily available.

Products of pyrolysis of polymers have been tested for identification purposes by gas vapor phase chromatography. Distinctive curve patterns have been reported for eight polymers[32]. This is an interesting application but its future is not clear as yet.

Although infrared is mainly useful for qualitative analysis of elastomers, it can also be used for quantitative determinations. Sands and Turner[33] have reported on the analysis of acrylonitrile copolymers for acrylonitrile. Their results are said to have a standard deviation of 1% with the figures obtainable in 15 minutes. However, this requires careful calibration and a special technique. Probably the main feature of their technique is the pressing of the samples between mica sheets.

DETERMINATION OR ESTIMATION

Although a single specific elastomer is usually in question, the difficulties of direct determinations suggest that an indirect approach should always be considered as a means of determining the polymer in an unknown sample. Even when a direct determination appears easy, the indirect method is a useful confirmation. This means the estimation of other materials present in the compound and subtraction of the sum from 100% in order to determine the elastomer by difference. Of course this means of estimation is fraught with many possible errors, but as a practical matter serious errors may occur only in very special cases. ASTM or British Standard Methods should be consulted for a list of the results which need to be summed up for subtraction from 100%.

Natural Rubber (*NR*).—For the estimation of natural rubber, the chromic acid oxidation method is suitable. It is given in both the ASTM and British Standard Methods. However, for more details the original publication[34] may be consulted. This method has also been reduced to microscale[35]. The principle of the method is to oxidize the rubber with chromic acid under suitable conditions to produce acetic acid. The amount of acid formed is equivalent to three isoprene units out of four, if calculated on a theoretical basis, although this is presumably only a fortuitous result of experimental conditions. The acetic acid is distilled and titrated after aeration to remove carbon dioxide.

To facilitate application of this procedure, it is possible to carry out the chromic acid digestion on a number of samples separately using reflux condensers. Then each flask containing the digested material can be transferred to the distillation apparatus for removal and titration of the acetic acid. The principal precaution in making use of this variation is to be sure that the digestion mixture is cold before the reflux condenser is removed. If this is not done, sufficient acetic acid will be lost to cause an error in the determination.

In some cases this procedure may be used for a qualitative indication of the presence of polyisoprene, either natural or synthetic.

Styrene-butadiene rubber (*SBR*).—This type of polymer has been identified qualitatively by digestion with nitric acid to form nitrobenzoic acid which is then reduced and coupled with a diazo compound to form a color. Also, according to the ASTM procedure the nitric acid digestion may be followed by a treatment with alkaline permanganate, the ether-soluble acids separated and titrated with alkali.

A much improved variation of this method also based on the formation of nitrobenzoic acid has been reported[36]. In this procedure the sample is extracted, digested with concentrated nitric acid under a reflux condenser overnight, the acid partly neutralized with alkali, and the nitrobenzoic acids extracted with

ether. After the ether is freed of nitric acid and nitrate, the nitrobenzoic acid is shaken out into 0.1 normal sodium hydroxide and light absorptions measured with a spectrophotometer at 265, 274 and 285 millimicrons. Styrene can then be calculated from these figures. Three wavelengths are chosen in order to detect interference.

This method, of course, depends entirely upon the styrene content of the polymer used in the unknown sample. Presumably, however, the analyst will have auxiliary information which will aid him in summing up final results.

Neoprene and other chlorine-containing polymers.—Assuming that a reliable identification has been made, neoprene and such chlorine-containing polymers as polyvinyl chloride can be estimated from determinations of the halogen. In the writer's experience a variation of Liebig's Lime Ignition Method is most serviceable. A good introduction to this procedure has been given by Kimball and Tufts[37]. These authors work with a mixture of calcium oxide and calcium nitrate but the writer and his coworkers have found that plain calcium carbonate has many advantages over the oxide-nitrate mixture. Ignition at 800° C in a hard glass tube in a manner similar to that used by Kimball and Tufts gives good conversion of the halogen to calcium chloride. The ignited mixture may be dissolved in dilute nitric acid, filtered if necessary, and halogen determined by Volhard titration using nitrobenzene to enclose the silver chloride and avoid the necessity of filtration.

Acrylonitrile elastomers (NBR).—These polymers can be estimated by determination of nitrogen by a variation of the Kjeldahl procedure. Here again the analyst must consider a comparison with the figure obtained by difference in order that he may arrive at a decision as to the type of acrylonitrile copolymer that has been used. These, of course, vary in their acrylonitrile contents depending upon the application for which the sample has been manufactured.

The Kjeldahl digestion may be carried out using copper as catalyst if sufficient time is given for the digestion after clearing, in order to convert all the nitrogen to the ammonium salt. Catalysts containing mercury permit shorter digestion times but have the disadvantage that the mercury must be precipitated as sulfide before the distillation of ammonia is carried out. An important point in the digestion to form the ammonium salt is that the heating must not be overdone. A loss in the ammonium salt occurs if the mixture becomes so concentrated that the boiling point is too high[38]. Better and more reliable control of the heating can be obtained with electric heaters than with gas burners. Many chemists have the impression that the Kjeldahl method is not suitable for determinations of this nature perhaps because Kjeldahl's original procedure was largely suitable only for amines. However, proper application of this method or its variations in detail make it possible even to determine ring nitrogen[39]. In the writer's experience Kjeldahl procedures have proven especially serviceable.

Butyl rubber (IIR).—As an alternative to the indirect determination of butyl by difference, the method of Galloway and Wake[40] may be employed. These authors use alternate treatments with concentrated nitric acid and light petroleum for a total of three complete cycles. The nitric acid destroys the diene groups present to reduce the molecular weight of the polymer and make it soluble in solvents like petroleum ether. After the solution in light petroleum is obtained, it is freed of nitric acid and evaporated. The residue is weighed after drying at 60 to 80° C. For the calculation of the original polymer the weight of the residue is multiplied by 1.03.

Kress[121] has improved on the work of Galloway and Wake to make it pos-

sible to determine the small but important amounts of butyl rubber which can cause layer separations when accidentally introduced into tire stocks, either of natural or styrene-butadiene rubber. After an initial treatment with nitric acid, the final dissolution of the diene polymer is accomplished with the aid of *tert*-butyl hydroperoxide. It is then possible to follow a detailed purification procedure and obtain the polyisobutylene representing the original butyl rubber for weighing.

Miscellaneous polymers.—A number of polymers are beyond the scope of this review although it is hoped that they will be covered at a later date. Examples of such materials which are of some commercial importance are the following: Thiokol, plasticized polyvinyl chloride, polyethylene, Hypalon (chloro sulfonated polyethylene), silicones, and fluorine polymers such as Teflon, Kel-F and Viton. Still others are synthetic "natural rubber" (polyisoprene), polybutadiene, and rubbers containing carboxyl groups.

SULFUR

FORMS

Before beginning the discussion of the various types of sulfur determinations, it is well to consider the various forms in which sulfur may be present in a vulcanized sample. These may be:

1. Free elemental sulfur or simply that left over as the element after vulcanization.

2. Sulfur of vulcanization; that is, the sulfur which has combined with the polymer. This combined sulfur may be present as crosslinked sulfur, sulfur which forms crosslinks between polymer chains and therefore contributes to the strength and modulus of the vulcanizate; or it may be chain sulfur, sulfur which is chemically combined in or with only one polymer chain and therefore may or may not contribute either to strength or modulus in the same order of magnitude as crosslink sulfur.

3. Accelerator sulfur. This refers to sulfur in such compounds as dithiocarbamates, thiuram disulfides, mercaptothiazoles and sulfenamide types where the sulfur is an appreciable fraction of the accelerator composition.

4. Sulfur in accelerator reaction products. Sulfur of this nature is difficult to specify because a considerable variety of accelerator reaction products have been identified and it does not seem unreasonable to suppose that there may be a number of others. For the purpose of rubber analysis, however, it is chiefly necessary to consider those reaction products which may not be extracted readily in order to remove them from consideration when combined sulfur is being determined. Such materials are likely to be the zinc salts of accelerators or more particularly the basic zinc salts which presumably might be formed by the reaction of zinc oxide with the accelerators present.

5. Sulfide sulfur. Sulfide sulfur (i.e., metallic sulfide sulfur) has been known to be present for many years and in fact has been recognized as a product of vulcanization almost ever since black stocks have been obtained with sulfur cures in the presence of litharge. What is not so well known, however, is the fact that sulfide sulfur may also occur in a somewhat different form. No thorough investigation of this has been made, but it is known that sulfide sulfur is decreased by extraction of a rubber sample. Since zinc sulfide (ZnS) or lead sulfide (PbS) would not be extracted with organic solvents (except after chemical reaction), it is presumed that that the sulfide may be present, for example,

in the thiol form where the SH group may correspond to the hydroxyl group of a basic salt as Zn(SH)(Stearate). Although the writer has been aware for some years that sulfide sulfur was decreased by extraction with organic solvents, little attention has been called to such decrease in the literature[41].

TOTAL SULFUR

Since the discovery of vulcanization by Charles Goodyear, no doubt the one determination most often used in the rubber industry has been analysis for total sulfur. A very important paper on the determination of sulfur was written by Wolesensky[42], who built on previous work by Kahane[43] to give a useful and reliable procedure. Wolesensky's paper was mainly about the oxidation of rubber samples to give complete oxidation of the sulfur to sulfuric acid while at the same time avoiding loss by spattering caused by the vigorous action. His paper is worth careful reading and consideration. Other work of comparable importance was that by Mackay[44]. Wolesensky succeeded in obtaining good oxidation by means of nitric acid and perchloric acids, and completed his determination by precipitation as barium sulfate. Mackay used nitric and perchloric acids but increased the oxidizing action by using fuming nitric acid and augmenting this still further by the addition of bromine. Mackay's paper is also well worth consultation by anyone who is interested in accurate sulfur determinations in rubber. Both Wolesensky and Mackay, of course, worked on natural rubber stocks in which the cures were somewhat different from present day industrial practice. For example, in the 22 stocks which Mackay cites the total sulfurs ran rather high—from 3.6% on up to 34.2% in the hard rubber which he included.

Although Mackay started with a procedure which employed benzidine as the precipitating agent, he later returned to the usual practice of precipitation as barium sulfate. This operation is so well known that discussion in this review does not seem necessary. Instructions can be found in several of the standard text books.

Kahane did some further work on the determination of sulfur which should perhaps be distinguished from his earlier reports cited by Wolesensky and Mackay. In this later paper[45] he admits that there were serious losses in the first procedure which he had proposed and suggests a somewhat longer procedure as a desirable substitute. The oxidation step in the first procedure was supposed to take place in 7–8 minutes. In the improved procedure given in the second paper this was increased to ½ hour with additional oxidizing action being obtained by the use of iodic anhydride. This procedure appears to offer no real advantages and seems to ignore some of the points demonstrated by Wolesensky and Mackay.

In transferring this older information on natural rubber to the analysis of synthetic polymers it has been the author's experience that SBR and NBR can be digested for oxidation of the sulfur in very much the same manner. Butyl rubber is considerably more difficult to oxidize, but the use of fuming nitric acid and longer digestion times make satisfactory determinations possible. Very careful safety precautions must be taken if polyisobutylene is the sample

or a major constituent. High molecular weight polyisobutylene will resist the action of nitric acid until the active concentration of perchloric acid is reached by evaporation. A sharp detonation will follow. Rehner and Holowchak[46] have reported on the determination of total and combined sulfur in butyl rubber. Their method was combustion in a Braun-Shell apparatus followed by precipitation with barium chloride. This avoids any great chance of explosion but requires the particular apparatus named.

Rehner and Holowchak used a temperature of 800° C in their furnace. More recently combustion at higher temperatures has come into consideration. Some advantages are claimed for applications to samples which include sulfur in compounding materials such as barium sulfate and calcium sulfate[47].

Although these high temperature combustions have considerable merit, there are some other methods which also have very interesting aspects. Luke has described a procedure[48] in which the precipitation of barium sulfate and its accompanying details are avoided. After digestion to form sulfuric acid, hydriodic acid is used to reduce all the sulfur to hydrogen sulfide, which is distilled into ammoniacal cadmium chloride and titrated iodometrically. This method potentially offers the promise of being very rapid. The technique as described by Luke is very difficult to carry out with precision. Much related information on a similar but improved procedure is contained in a paper by Bethge[49], who has taken rather elaborate precautions to insure that the titration of the hydrogen sulfide will be accurately controlled.

Another very interesting development has been reported by Kress[50]. This is a micro determination in which the sample is oxidized roughly as described above with nitric acid and perchloric acids. Considerable time is gained by precipitating the sulfate as lead sulfate and measuring it by ultraviolet absorption at 270 millimicrons after the precipitate has been converted to the lead chloride complex. This appears to be a promising method, although for samples of micro size it becomes very important to insure that the sample represents the bulk of the material being analyzed.

In the laboratories of the United States Rubber Company, the writer and his colleagues have developed a method for total sulfur which has rather general applicability. Up to the present time it has been used on a small macro scale but would probably permit reduction to micro scale without serious difficulties. Since the procedure has a number of interesting advantages, it will be described here in simple outline.

Oxidation of both natural and synthetic rubber samples is done mainly with nitric acid under reflux. Bromine is added where samples are crumbly and may react with too much evolution of heat if treated directly with ordinary concentrated nitric acid. Fuming nitric acid is used if butyl rubber samples are being analyzed. A small amount of phosphoric acid is used in the oxidation mixture for safety purposes. In cases of samples which are very difficult to oxidize, the presence of the phosphoric acid reduces the likelihood of serious explosions as the evaporation following the nitric acid digestion causes the production of an active concentration of perchloric acid. In other words, the phosphoric acid is used as a diluent for safety purposes in much the same way as in metallurgical analysis.

After the digestion with nitric acid has proceeded completely enough and evaporation is to take place to clean up residual organic matter by the action of perchloric acid, the flask is removed from the original reflux condenser and the condenser replaced with a simple evaporation head as shown in Figure 1.

When the organic matter has been completely oxidized, the determination

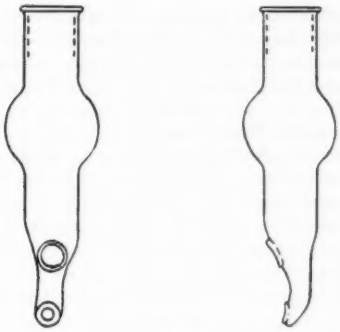


FIG. 1.

is completed by evolution of the sulfur as hydrogen sulfide and its titration iodometrically. Before reduction with hydriodic acid, which is used as the reagent, it is absolutely essential to remove the last traces of nitric acid. This is done by two evaporations with hydrochloric acid and is similar to the same step as described by Bethge[49], who used hydrobromic acid.

The reduction and distillation of the hydrogen sulfide is done in the apparatus shown in Figure 2. The hydrogen sulfide is distilled into ammoniacal zinc acetate. Cadmium is not used, since its sulfide is reported to be light sen-

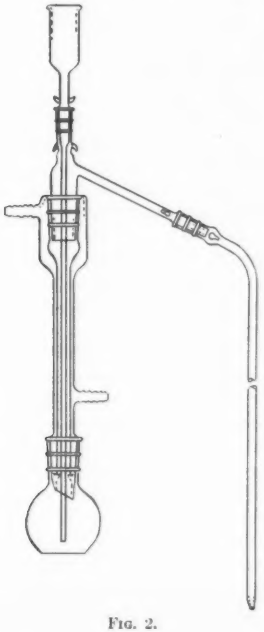


FIG. 2.

sitive[51]. No carrier gas such as nitrogen or carbon dioxide is needed. Some hydrochloric acid distills and aids in the transfer. The hydrogen sulfide is received in ammoniacal zinc acetate contained in a beaker. At the end of the distillation the delivery tube is disconnected from the apparatus and used for stirring pruposes. The pH of the solution is reduced to between 2 and 3 with acetic acid. Since Fales and Ware[52] have shown that zinc sulfide can be quantitatively precipitated in a pH range of 2 to 3, it is evident that it should be stable in this range once formed. This pH is sufficiently low that the oxidation of hydrogen sulfide according to the reaction $H_2S + I_2 \rightarrow 2HI + S$ will take place quantitatively and with a minimum of side reactions. An excess of standard iodine solution is then added and the pH reduced with hydrochloric acid to break up the zinc sulfide. Excess iodine may then be titrated with standard sodium thiosulfate. The precision and accuracy of the method can be demonstrated with potassium sulfate as a standard substance.

FREE SULFUR

The term free sulfur has been used in two ways. One is the sulfur in the acetone extract, the other is the free, uncombined sulfur existing as the element. The acetone extract sulfur, of course, was understandable as free sulfur many years ago before the use of sulfur bearing accelerators became prevalent. Since that time the term has continued in use, although it must be confusing to many people not familiar with the custom.

The sulfur in the acetone extract may be determined by any of the methods of oxidation discussed under total sulfur. However, because of the various forms of sulfur present in an extract, the significance of a result can be interpreted only in relation to other facts known about the sample being analyzed.

The two usages mentioned above for the term "free sulfur" are exemplified in ASTM methods, the current number for the group being D297–55T. There, besides the procedure for sulfur in the acetone extract, is given the other and more important method from the modern point of view: the determination of free elemental sulfur by reaction with sodium sulfite in a direct treatment of the sample without previous acetone extraction. This method is that of Oldham, Baker, and Craytor[53]. Since these authors cite very briefly other methods which might be considered of some importance, no further mention of them will be made here.

No other methods besides the acetone extract and sulfite digestion procedures are known to be in any general use. As a matter of comparatively recent interest, however, it might be mentioned that free sulfur can be determined by polarographic methods[54].

Although the paper by Oldham, Baker, and Craytor is of prime importance in respect to the determination of free elemental sulfur, some further discussion seems highly desirable. There is no question that the method is good as written, but many variations are possible, and some precautions should be carefully observed. In principle the free sulfur in the sample reacts with sodium sulfite to form sodium thiosulfate, which is titrated iodometrically. In order to carry out this titration, it is necessary to inactivate the excess sulfite by reaction with formaldehyde[55]. This titration is not difficult in the absence of interferences. Other details of the free sulfur determination warrant some comment. To begin with, the sample must be as carefully prepared as for acetone extraction. That is, it should be thinly sheeted to a thickness of approximately $\frac{1}{2}$ mm. (about 0.020 inch). In cases of masterbatches it is especially necessary to have

this sheeting done shortly before the sulfite digestion is carried out. Large crystals of sulfur, if not broken into fine particles, will not diffuse and react in a reasonable length of time with the sulfite. Sodium sulfite solutions oxidize readily from contact with the air. When the sodium thiosulfate is present also, it is rapidly attacked by oxygen of the air, and the resultant final free sulfur figure is thereby in error on the low side. This can be avoided in a practical way by using 10 mg of hydroquinone per liter of sulfite as antioxidant. With this preservative if the solution is not shaken or stirred vigorously in use, it should be good for approximately a week. The sulfite solution may be used in much smaller quantity than specified by Oldham, Baker, and Craytor or the ASTM procedure, and at least in certain special cases the digestion time may be greatly shortened. For example, with a simple mix of 100 pale crepe and 1 of sulfur it can be demonstrated that 20 ml sulfite will remove the free sulfur from a suitable sheeted 1 g sample in 15 minutes. In cases such as this as well as many others, the soap and paraffin and the precipitation step can be completely omitted. Some soap is formed from the reaction of the alkaline sulfite solution with fatty acid in the sample. Thus, sufficient wetting action is obtained without the addition of extra soap. Paraffin is not necessary unless boiling is active, and boiling can be avoided if the solution is kept near a boil and occasionally stirred. The necessity for the precipitation, of course, depends on what accelerators are present, and filtration may be required in most cases, although accelerators such as the aldehyde amines and guanidines need not be removed. Thiazoles and their derivatives can be taken out of the sulfite solution by shaking with normal butyl alcohol.

SULFIDE SULFUR

The determination of sulfide sulfur is not made ordinarily as a routine analysis. It is to be expected mainly of interest in connection with studies of the theory of vulcanization[56,57]. Sulfide sulfur was originally determined by H. P. Stevens in 1915[58]. Stevens decomposed the sulfide by soaking the rubber sample in ether and hydrochloric acid and swept over the resulting hydrogen sulfide with a stream of carbon dioxide into a lead acetate solution. The lead sulfide was filtered off, then shaken with an excess of standard iodine solution and the excess iodine titrated. This procedure is somewhat troublesome to carry out but does seem to give satisfactory results.

Some time after Stevens' original procedure another worker suggested treatment of the sample with hydrochloric acid in acetic acid, rather than in ether. The acetic acid behaves as an organic solvent and helps carry the hydrochloric acid into the rubber in much the same way as ether. However, it is much less volatile and is, therefore, not carried over in the sweeping in the same way that ether is transferred. The identity of the first person to use acetic acid is obscure, but mention of its use was made as early as 1920 by Pearson[59].

Sulfide sulfur may now be determined much more easily than these early references indicate. The apparatus shown in Figure 2 may be used. In carrying out the determination, a sample of suitable size is placed in the flask and treated with a 1:4 mixture of concentrated hydrochloric acid and glacial acetic acid. After a short warming and soaking period, the acid is brought to a boil and the hydrogen sulfide driven over into ammoniacal zinc acetate solution which has already been placed in the receiving beaker. The final titration step is carried out as indicated above under the total sulfur determination.

If the heating and distillation of the hydrogen sulfide are carried out in

exactly the right way, no carrier gas is necessary. The HCl present serves this purpose and, in addition, seems to prevent the oxidation of hydrogen sulfide by any air present. Air may be used for sweeping purposes if desired.

Although the above procedure works well and accurately according to the author's personal experience, another possibility for the receiving solution is the use of sodium hypochlorite[60]. Since the sulfur is thereby oxidized to sulfate, a greater number of hydrogen equivalents are required. This may be considered as making the titration more sensitive.

COMBINED SULFUR

The determination of true combined sulfur or polymer combined sulfur has been one of the principal aims of analytical chemists working on rubber. Very little has been published on the subject. ASTM procedures do not attempt it,

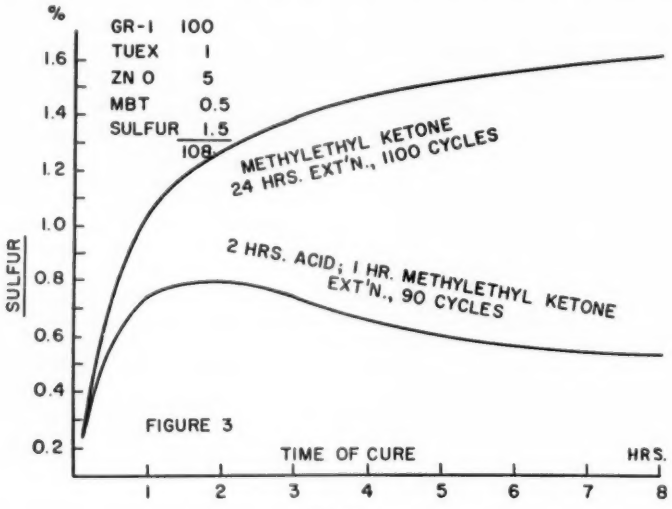


Fig. 3.

but refer to organic sulfur as the closest approach. This "organic sulfur" is referred to as the sulfur which is not removed during acetone extraction or by total extraction, that is, extraction with a mixture of 32 parts of acetone and 68 parts of chloroform by volume. However, there is a way of determining true combined sulfur or polymer combined sulfur with some assurance, although it must be admitted that there is no other way of checking results so obtained.

By combining the information just given briefly in the preceding sections on the forms of sulfur and on the determinations of total, free, and sulfide sulfur, it is possible to arrive at a method which has given informative results in the writer's experience for several years. The determination is carried out according to the following outline:

1. A sample which has been sheeted on a mill or otherwise prepared as if for extraction, is treated on a steam plate with a portion of the acetic acid-hydro-

chloric acid mixture used for the sulfide sulfur determination. The acid not only breaks up sulfides and drives off hydrogen sulfide, but also decomposes accelerator reaction products normally containing sulfur and makes them more readily extractable.

2. Extraction with acetone or methyl ethyl ketone.

3. Determination of sulfur in the extracted residue by the same procedure as used for total sulfur.

This type of approach can be used for natural rubber, synthetic rubber of the SBR type, and butyl rubber. A striking example of its application to butyl rubber is shown in Figure 3. There the upper curve shows results on the combined sulfur as obtained after methyl ethyl ketone extraction as recommended by Rehner and Holowchak[46]. The lower curve shows results obtained by the procedure outlined above. It will be noted that there is a wide difference between the two curves. In the lower one a peak is observed at around two hours curing time, which corresponds to the peak in physical properties not indicated in any way by the upper curve.

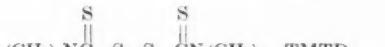
Presumably, the same general method could be applied to neoprene and nitrile type copolymers if the proper extraction solvent could be selected.

ACCELERATORS

Accelerators are of great economic importance to the rubber industry. They not only shorten vulcanization time from hours to a fraction of an hour, but they also have important effects on the physical characteristics of stocks in which they are used. These influences on physical properties are important in relation to the final use of rubber products.

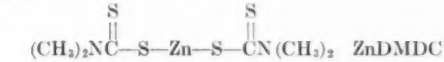
Accelerators in general are made up of several chemical types. The important classes are aldehyde-amine condensation products, thiurams and dithiocarbamates, thiazoles, guanidines and sulfenamides. The aldehyde-amine condensation products are not usually clear-cut chemical compounds and therefore are not easy to detect or identify. However, the analytical literature on accelerators seems to indicate that aldehyde-amine accelerators are of less importance as time goes on. Typical formulas for the other classes are as follows:

Thiuram:



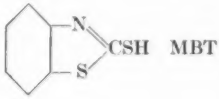
TMTD

Dithiocarbamate:



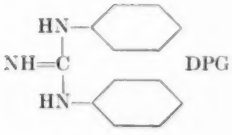
ZnDMDC

Thiazole:



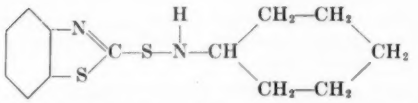
MBT

Guanidine:



DPG

Sulfenamide:



In many cases an identification of the accelerator is sufficient for a compounder in attempting to duplicate an unknown stock. If the general composition has already been determined except for the accelerator, it is fairly easy to run a few cures to estimate the optimum proportion of accelerator to be desired. In cases where more than one accelerator is used, curing tests may necessarily become so numerous that it is much more important to arrive at quantitative results by analytical means.

Early work on the analysis of rubber for accelerators is difficult to summarize. This is because the chemical reactions taking place during vulcanization have not been well known. Even today the chemistry of accelerators is obscure. Therefore, in retrospect it is easy to understand that early analytical references involved a variety of approaches: qualitative tests, a few limited quantitative procedures, and reports on attempts at satisfactory separations.

One of the better ways for a chemist to become familiar with accelerator chemistry would be to read a number of earlier references in that analytical field[2,61,62,63,64].

A considerable amount of important work from an analytical point of view is reported by Shimada[65]. Most of Shimada's work was concerned with color tests for accelerators. His principal reagent was cobalt oleate, the preparation of which is important. Slepushkina[64] gives specific information. Tests with a few other metallic salts were included in Shimada's work, which was published from 1932 to 1938. More recently Schaefer[66] reported in detail on tests with copper sulfate or acetate. He found that significant differences could be observed if the test mixtures were allowed to stand 3 hours or longer.

During the period when Shimada was publishing his work, a few special procedures appeared from other authors for the quantitative determination of certain accelerators. For 2-mercaptobenzothiazole titration with alkali[67] or with silver salts was recommended[68]. Gravimetric determination as the silver salt was also suggested[69].

Titration with iodine to form the disulfide was condemned as inaccurate[67,70]. This was unfortunate because there is a reasonably accurate procedure by which 2-mercaptobenzothiazole can be titrated with iodine[71]. Since this procedure has not been published elsewhere, it is desirable to outline it here: Dissolve about 0.1 g of 2-mercaptobenzothiazole containing sample, accurately weighed, in ten ml of glacial acetic acid. Dilute with 150 ml of water containing sufficient sodium hydroxide to produce a pH of 4.0 to 4.8 (NaOH equivalent to about $\frac{1}{3}$ the acetic acid). Titrate immediately with 0.02 normal iodine with rapid stirring and using starch as indicator. The end point under favorable conditions should be certain to one drop of the iodine solution. Under no circumstances should the diluted solution be allowed to stand more than a few seconds before titration. There is a tendency for the 2-mercaptobenzothiazole to crystallize out and thus make the reaction with iodine incomplete.

A variation of this procedure can also be used for the analysis of benzothiazolyldisulfide (MBTS). In this case the sample can be dissolved in the acetic acid, reduced to 2-mercaptobenzothiazole by passing in hydrogen sulfide, and titrated with iodine as above after the excess hydrogen sulfide has been

boiled out. This might be considered an extension of the work done by Robinson[72] who made the reduction in alkaline solution and finished the determination by weighing the precipitate of 2-mercaptobenzothiazole. During this same period of the early development of accelerator analysis, a small amount of other quantitative work was reported. The guanidines because of their basic nature were determined volumetrically by titration with hydrochloric acid in water solution[73]. This same basic character was also used as an aid to extraction in a preliminary step prior to precipitation and weighing as the picrate[74]. Dithiocarbamates were tested for by reaction with copper salts, and presumably this could be made roughly quantitative as a reversal of the determination of copper traces by the colorimetric methods existing at that time[75].

In later years after World War II an increase in the quantity and quality of analytical work on accelerators took place. This was no doubt due to the application of two new techniques which had become available: ultraviolet and visible spectrophotometry[76,77,78,79] and chromatographic or adsorption-elution analysis[80,81,82,83,84,85,86].

Ultraviolet absorption is an especially sensitive means of detecting and identifying a number of rubber chemicals. It is especially useful for analytical work in regard to accelerators but may be applied to antioxidants and to a few other soluble organic materials as well. Anyone wishing to become acquainted with the earlier work might consult a paper by Jarrijon[77], but then it would be desirable to pass on rapidly to a report by Kress[78], which is a good basic reference. Seven typical accelerators were studied. Thiazoles, thiurams, and guanidines were included, but no zinc salts were covered. Somewhat later Kress and Stevens Mees[79] reported on a more complete approach whereby acid extracts or alkali extracts were given solvent treatments to separate curing agents for identification by ultraviolet absorption. This was carried out on 2 g samples in a total time of about 4 hours. It was noted that oximes and retarders such as salicylic acid or phthalic anhydride might be detected also.

For best results with ultraviolet absorption it is desirable to have the material to be identified and determined in a relatively pure state. This is also true in most other cases where various tests may be applied. This need for purification and separation led to a variety of applications of chromatographic analysis. Bellamy, Lawrie, and Press[80,81] gave this a good start. Their work was followed and extended by Mann[82], who worked on acetone extracts from 10 g samples, employing chromatographic separation to prepare material for identification by infrared absorption. His paper gives a good discussion of accelerator chemistry and transformations during cure. Parker and Berriman[83,84,85] went further with a study of the properties of silica gel/celite columns. They emphasized the necessity of extractions under certain specific conditions to avoid decomposition of the accelerator during the extraction step. They succeeded so well that they stated as little as 0.01% of dithiocarbamate could be detected in 0.4 g of rubber. The references that they cite appear particularly useful for anyone wishing to study background work more thoroughly.

In much of this chromatographic work a rather large volume of solvents and a considerable expenditure of time are necessary.

It would seem that paper chromatography might afford a means of considerable saving of solvents and possibly also of time. Comparatively recently Zijp[86] has reported on such application. He uses a rather large amount of sample, 17 g in all, in a scheme which is intended to be applicable to a completely unknown sample. The overall time required is rather long, since the

first step is an eight hour extraction in a Soxhlet apparatus. This does not compare favorably with the time of four hours cited by Kress and Stevens Mees[79]. As this field of accelerator identification is reviewed, it leaves one with the impression that an expert in the field might possibly consolidate the facts reported in several papers to form a plan of analysis which might be still more rapid and satisfactory in general than the procedures now available. Undoubtedly some decision would need to be made as to whether or not ultraviolet absorption would be an essential part of the plan. Spectrophotometers are increasing in numbers but still are not available in many locations where they might be needed.

Another rather general scheme of analysis which might be mentioned is that of Brock and Louth[87]. They worked with samples of from 15 to 20 g and included a feature not mentioned heretofore, that is, distillation of an amine from the accelerator and its identification by the x-ray powder diffraction pattern of the hydrochloride[88].

Besides spectrophotometric methods and x-ray diffraction some other instrumental methods are of interest. Proske[89] and Poulton and Tarrant[54] have described some work on the polarographic behavior of sulfur and accelerators. English[90] has described the polarographic determination of dimethylamine. It is to be expected that a similar procedure could be applied to other amines which might be obtained from rubber accelerators.

Conductometric titrations have been made on a variety of accelerators by Scheele and Gensch[91]. Lorenz and Echte[92] have reported on the conductometric titrations of 2-mercaptobenzothiazole and its zinc salt. Their work also included the reduction of benzthiazolyl disulfide to 2-mercaptobenzothiazole with stannous chloride in order to prepare it for conductometric titration. Quanitative determinations of thiurams and dithiocarbamates are possible by causing evolution and distillation of carbon disulfide, which may be trapped and measured by means of ultraviolet absorption[93] or in favorable cases by iodine titration[94].

ACTIVATORS

Directly after the principal features in vulcanization—type of elastomer, sulfur amount, nature and amounts of accelerators—comes the question of activators. These are materials which might be said facetiously to accelerate the accelerators. The knowledge of such materials began with recognition of the fact that such compounds as litharge and zinc oxide aided vulcanization. Soon this was coupled with the fact that a fatty acid was also helpful. Since lead oxide always produces black stocks, its use has gradually diminished. Zinc oxide is now to be expected as an additive in almost any sample that comes to hand. The fatty acid is generally considered to react with the metal oxide to form a salt of the metal or a soap which is soluble in the rubber, thereby raising the concentration of the active materials if one is to assume the operation of the law of mass action. Stearic acid is the most frequently used fatty acid, but lauric acid is also important, and other acids or mixtures are not to be neglected as unworthy of consideration. The metal oxide and acid may be combined before addition to the rubber, as for example in the use of zinc stearate or laurate.

From a practical point of view the determination most often required in connection with activators is for zinc. Sometimes the determination of lead may be needed, and once in a while some investigation of the fatty acid may be desirable.

ZINC COMPOUNDS

In order to prepare a sample for the determination of zinc it should be wet ashed; that is, the organic matter should be destroyed by oxidation with acids or mixtures of acids rather than by dry ashing as commonly practiced. Zinc, if reduced to the metal during ignition, is somewhat volatile. In the presence of halogen, as in neoprene, chances of loss are greater[95]. Much information on the destruction of organic matter by wet oxidation has been published by G. Frederick Smith[96,97,98]. His procedure may be applied to samples as large as 10 g or even larger. Nitric and sulfuric acids, alone or together, are used for the main destructive process, and perchloric acid is used for the clean-up of residual organic matter not easily or completely oxidized by the first two acids. No work of this nature should be undertaken by anyone who is not familiar with the necessary safety requirements. Smith's papers should be read with care in order to learn the necessary precautions. Useful variations in the way the acids are applied are possible. Nitric acid may be used in the ordinary concentrated form, as the fuming acid, or as a solution saturated with bromine. Concentrated nitric acid sometimes gives the fastest initial attack on a sample, especially if it is well cured and has been crumbled by passing through a tight mill. The presence of bromine slows up the action of nitric acid, apparently because the bromine reacts first, and thereafter the nitric acid does not react so rapidly with the brominated product. Fuming nitric acid is useful at times, especially in the initial attack on butyl rubber samples. Fuming acid is not necessarily more reactive than concentrated nitric acid because of its lower boiling point. At times it is advantageous to use mixtures of nitric acid and sulfuric acid. If there is the slightest doubt as to the speed of reaction in any particular case, conditions should be tried experimentally with a few milligrams of sample behind a safety shield. Thereafter, if the sample is increased on the basis of the apparent safety of the initial small scale test, it must be remembered that the heat of reaction is more concentrated as samples become larger. This in itself, increases the chance of an explosion as sample weights are multiplied.

As the final step in the destruction of organic matter, the solution would be evaporated to fumes of sulfuric acid or perchloric acid as the case might be. This evaporation would dehydrate any silicious material and on dilution would leave the zinc in solution as the sulfate or perchlorate. After filtering off any insoluble, several methods might be used for the determination of the dissolved zinc.

The method most commonly used is titration with ferrocyanide. This can be carried out using either uranyl nitrate or ammonium molybdate as outside indicators on spot plates. Although such titrations are difficult to carry out, they may be done with fair accuracy and speed by one experienced in the art. For example, half of the solution may be first titrated in order to arrive at an approximate end point, then the other half added and the titration continued to arrive at a more accurate end point. This may be facilitated by having a number of indentations on the spot plates ready with drops of the indicator solution and then titrating beyond the end point with a series of small, known increments of the ferrocyanide solution. By titrating in this manner, it is possible to go beyond the end point to a distinctly recognizable change in color and then correct back to the nearest whole increment where the end point color change can be perceived. This manner of operating, in the hands of an experienced analyst, is more rapid and accurate than would at first be expected.

However, in many respects an internal indicator is more satisfactory because it is a closer approach to common practice and experience. Tyler[99] has re-

ported on the use of *p*-ethoxychrysoidine indicator and has given a good description of its application in the determination of zinc in rubber compounds. His paper is a noteworthy reference for the rubber analyst, but there is one detail which is in some doubt. That is the temperature of the titration, which appears to be somewhat too high. Sturges[100], during his study of the potentiometric determination of zinc, observed decomposition to form hydrocyanic acid if ferrocyanide were added above 70°. As a counter measure he precipitated at room temperature and allowed the precipitate to stand 15 minutes before a back titration with ceric sulfate. The writer has also noted the odor of hydrocyanic acid while attempting titrations in the range of 70° to 90°. On the other hand, a temperature of 50° to 60° gave excellent results. Richardson and Bryson[101] made a thorough study of the ferrocyanide titration of zinc. In their work, which was with diphenylbenzidine as indicator, they concluded that the titration should be a direct one at room temperature. As other investigators had previously found, their results were slightly low, approximately 0.8% for the range of 30 to 300 mg of zinc. In order to compensate for this they suggested as others had done previously that the ferrocyanide be standardized against known amounts of zinc.

Richardson and Bryson also pointed out that old ferrocyanide solutions may contain too much ferricyanide. This is important because it may mean that the potential change at the true end point is too low to bring about a suitable change in the color of the indicator. Thus the situation may arise where end points are poor and it is not easy to ascertain whether the cause is a poor indicator solution or a poor standard solution of ferrocyanide which may have developed too high a ferricyanide content from air oxidation.

Some newer indicators have been reported which appear to be improvements over 2-ethoxychrysoidine. These are the base 3,3′-dimethylnaphthidine[102] and the corresponding sulfonic acid[103]. With the base compound best results are obtained when excess ferrocyanide is added and then titrated back with standard zinc solution. The corresponding sulfonic acid, the preparation of which is described by Belcher, Nutten, and Stephen[103], can be used for direct titrations. Excellent results are obtained even in unusually dilute solutions.

Although the ferrocyanide titration is the leading method for the determination of zinc, there are some other methods with points of interest. The ferri-ferrocyanide equilibrium may be used in such a manner that zinc is precipitated as the ferrocyanide, and yet the well known advantages of the iodine end point can be obtained[104].

Another method which sometimes is considered favorably because of speed and ease of precipitation of the zinc in the form of a compound which can be readily titrated, is the iodate method of Jamieson[105]. In this method the zinc is precipitated as $ZnHg(CNS)_4$. The end point is the disappearance of iodine color from a small volume of chloroform which is shaken with the solution as the iodate titration proceeds.

Zinc has also been determined in compounded rubber by the use of the polarograph[106]. Such an instrument, because of its sensitivity, means that relatively small samples can be used and therefore wet ashing may be employed with somewhat more speed and greater safety. Separations may not be required and other elements can possibly be estimated in the same solution.

FATTY ACIDS

Fatty acid is seldom determined except on raw polymers of the SBR type; however, special cases may arise where some investigation of the acid is desir-

able. Separations take place in the chromatographic procedures as indicated above under the discussion of accelerators. Fatty acids can be determined by spectrophotometric methods in the application of the hydroxamic acid reaction[107,108]. Identification can be made by x-ray diffraction analysis of amides and silver salts[109] and by the determination of dissociation temperatures of urea complexes[110]. In this latter case the determination of the dissociation temperature is run just like that of a melting point in a capillary tube and is therefore relatively simple and easy.

ANTIOXIDANTS

By adjusting the several factors making up the curing system of a given stock, it is possible for a rubber compounder to obtain good aging qualities. This means the proper balance between the amount of sulfur, time of cure, type of accelerator, and the combination of activating material used. Analyses in regard to these materials have been discussed in the foregoing pages. However, in spite of the fact that aging is influenced by the adjustment of the curing system, the service life of a rubber article can be greatly extended by the use of antioxidants.

In a general way antioxidants are made up of two chemical classes: secondary amines and substituted phenols. Typical examples of amines are N-phenyl-2-naphthylamine and N,N′-diphenyl-*p*-phenylenediamine. The substituted phenols are less numerous and perhaps more difficult to exemplify. An example of this type of compound is 2,6-di-*tert*-butyl-4-methylphenol.

The amine type antioxidants are much more effective in prolonging the life of rubber stocks than the substituted phenols. However, they have the general property of causing discolorations. That is, as they themselves are oxidized, they form yellow to dark brown products which stain materials with which they come in contact. The substituted phenols are practically free of this disadvantage of staining, but they are much less effective in their protective action than the amine antioxidants.

The development of analytical methods for antioxidants has followed a somewhat similar historical pattern to those for accelerators but later in terms of years. Only a small amount of work was published prior to World War II. Endoh[111] described a number of color tests made on the amine antioxidants with various oxidizing reagents: nitric acid, ammonium vanadate, arsenic acid, selenic acid, and potassium persulfate. These reagents are helpful in a given case where one wishes to find out whether an antioxidant is present or absent. They are not very useful, however, for the identification of unknown antioxidants because the action of oxidizing agents is a general one, and in many cases the colors produced are quite similar. It is to be expected that other oxidizing agents not listed by Endoh would also give similar colorations in a general way. It is of interest to note that the amine antioxidants are rather closely related to the oxidation-reduction indicators which are now so valuable to analytical chemists.

Craig[112], in a paper on the determination of diarylamines in rubber published in 1937, summarized briefly but adequately the situation in regard to the determination of antioxidants as it stood at that time. Craig's paper is probably the first important publication on the determination of amine antioxidants. He distilled the amine from the rubber with super-heated steam at 170° to 180°, separated it as a hydrochloride, and finally weighed it as the original amine after hydrolysis. The principal other paper on the quantitative determination of antioxidants which appeared before World War II was by Howland and

Hart[113]. These workers determined antioxidants by measuring the induction period produced in connection with the oxidation of specially prepared turpentine. Apparently the necessity for the special apparatus employed has prevented this method from being used more generally. After World War II much more rapid progress was made in regard to antioxidant analysis. A good deal of it was associated with similar work on accelerators since any method of separation from rubber would involve both accelerators and antoixidants. A number of papers have already been cited in this connection[82,83,84,86,87]. Besides these, there is one other paper by Poulton and Tarrant[54] which includes important information on antioxidants, although the title refers only to the polarographic determination of sulfur.

A few other papers should be added to this list to round out the group on antioxidants. Burchfield and Judy[114] described further color reaction of the amine antioxidants. Schneider[115] made an investigation of oxidations with various reagents on chemical structures more or less closely related to the antioxidants. His discussions and references are especially interesting. As in the case of accelerators, applications of chromatography and ultraviolet absorption analyses came into use. An important paper in this respect was the one by Hively, Cole, Parks. Field, and Fink[116]. They combined elution chromatography on the acetone extract with ultraviolet absorption to determine several of the more important antioxidants. This important work with ultraviolet absorption, which began largely with Banes and Eby[117], was given an important twist by Wadelin[118] in regard to the determination of phenolic antioxidants. He used the change in peak height between neutral and alkaline solutions as a means of measuring the substituted phenols.

Very recently applications of paper chromatography for the determination of antioxidants have been described by Zijp. He first reported on the determination of phenyl naphthylamines[119]. In this paper, which appears to be fairly important, he cites previous related references, including the one which tells how to make the completely acetylated filter paper which he employed for his chromatographic separations. In addition, in this same paper he outlines a general scheme for a 1 to 2 g sample. An aliquot portion of an extract is applied to the filter paper, chromatographed, and the separated antioxidant spots cut out for a colorimetric determination. The color is produced by coupling with freshly diazotized sulfanilic acid. In the second paper of this series[120] on phenylene diamine derivatives, approximately the same procedure is followed. The color in this case is produced by reaction with benzoyl peroxide.

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ELASTOMERIC PROPERTIES OF BUTYL RUBBER

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I. INTRODUCTION

On first thought, the properties controlling the behavior of high molecular weight substances would appear to be so overwhelmingly numerous as to defy consolidation and simplification. However, upon analysis, it can be seen clearly that they all reduce to areas of consideration which make up a relatively small group. For elastomers, such a grouping might be as follows.

Size
Shape
Order and Disorder
Composition
Crosslinked Network
Response to Deformation
Degradative Reactions

This reviewer does not intend to imply that each area can be considered mutually exclusive of any of the others. There is ample evidence of considerable interaction between these areas. Moreover, it is not intended to imply that the approach to elastomeric problems is utterly simple. The complexity within any one of the areas mentioned is well known from the literature on polymers. However, it is suggested that a grouping or classification such as given here can assure a greater clarity of concept and objectivity of analysis and experiment in approaching otherwise obtuse and complicated polymer problems.

As each new polymer material comes under research scrutiny in this sense, the general "laws" governing polymer behavior are clarified and extended. This is a result of the fact that each new material usually provides features which invite and encourage research, particularly where uncertainty exists. The case of butyl type polymers will be reviewed in this sense with two purposes in mind: (1) to define and correlate the knowledge derived from butyl research which has contributed to a better understanding of the principles of polymers, and (2) to suggest (often by inference) areas where potentially fruitful research in the same direction is still possible.

This review will consider butyl polymers beyond the polymerization stage. Except where necessary to develop the proposed objectives, the chemistry of polymerization will not be considered. A number of references are recommended to the reader interested in the polymerization aspects[1,2,3,4a].

No attempt will be made in this review to consider butyl end uses or the compounding and technological information associated therewith. Some exception to this restriction will be made when the particular property under consideration warrants it. Rather, this review will attempt to show how a development of the basic knowledge of polymer behavior can be put to use in the solution of technological problems.

Relative to end use information on butyl, the reader is referred to two extensive and well coordinated manuals on transport and nontransport products. These manuals, available from the Enjay Company, Inc. are titled "Enjay Butyl-Volumes I and II" and "Enjay Butyl for Tires".

Butyl has been defined as an olefin-diolefin copolymer having a molecular weight (Staudinger) of at least 15,000 and an iodine number of 1–50. The olefin used in commercial butyl polymers to date is isobutylene. Isobutylene represents the major portion of the butyl chain. Many of the properties of butyl polymers are dependent therefore on this monomer and its behavior in the large molecular structure. In view of this, a considerable portion of the research referred to in this review will be in terms of isobutylene polymers. It will be readily recognized that transfer of this knowledge to the copolymers with diolefins is legitimate.

This reviewer has chosen to select certain areas of research on butyl and develop them in some detail as fits their bearing on the objectives of this review. Unfortunately, many excellent pieces of research will be omitted or even overlooked in a work of this type. Although practically all of the material contained in this review is available to the reader in one form or another in the literature, it is hoped that this reviewer's part in drawing it together around the central theme of butyl polymers and their role in advancing research may be a helpful and integrated guide.

II. BUTYL POLYMERS

Grades, specifications and special properties.—Currently, there are nine grades of Enjay Butyl polymers available commercially. These grades and their quality control physical properties are shown in Table I. Included also for general information are mole per cent unsaturation and viscosity average molecular weight data. These are typical values and are not included in the specifications. It will be noted that the nine grades represent a range of rates of vulcanization, as judged by modulus and a range of viscosities as measured on the Mooney Viscometer. The grades containing a 6 in the numerical code contain a non-staining antioxidant. The standard grades of polymer contain phenyl-2-naphthylamine as a stabilizer while the nonstaining grades contain N-lauroyl-*p*-aminophenol. The stabilizer content is usually about 0.2 per cent. The range of butyl polymers thus offers materials for research and technological experiments which cover two of the more important parameters of polymer behavior, namely chemical activity and molecular weight. Furthermore, the availability of the related polymers of polyisobutylene (Vistanex) over a wide molecular weight range broadens the scope of useful research with this type of polymer.

Within a class, the butyl polymers can be considered as a homologous series differing only in the average molecular weight and the molecular weight distribution. A molecular weight distribution plot for Enjay Butyl 215 is shown in Figure 1. The plot shows the per cent cumulative weight for the entire polymer and the distribution or group frequency in units of molecular weight of 50,000. The measured molecular weight is found to be $\bar{M}_v = 370{,}000$. The molecular weight calculated from the sum of the molecular weights of the fractions is found to be $\bar{M}_v = 350{,}000$. There would be three polymers in this class; Enjay Butyls 215, 217 and 218. Their viscosity average molecular weights would be about 350,000, 400,000 and 450,000, respectively. Corresponding plots of molecular weight distribution for the two higher molecular

TABLE I

GENERAL PROPERTIES OF ENJAY BUTYL POLYMERS

	Enjay Butyl 035		Enjay Butyl 150 and 165		Enjay Butyl 215		Enjay Butyl 217		Enjay Butyl 218* and 268		Enjay Butyl 325 and 365	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Viscosity range												
ML 212° F at 8 minutes	41	49	41	49	41	49	61	70	71	—	41	49
Viscosity average molecular wt.[a]	350,000		350,000		350,000		400,000		450,000		350,000	
Mole % unsaturation[a]	0.6–1.0		1.0–1.4		1.5–2.0		1.5–2.0		1.5–2.0		2.1–2.5	
Tensile strength, psi												
40′ cure at 307° F	2600		2500		2400		2400		2400		2300	
Ultimate elongation, % minimum	700		650		550		550		550		500	
Modulus, psi @ 400% elongation												
20′ cure at 307° F	400	590	590	770	770	950	770	950	770	950	950	1125
40′ cure at 307° F	650	900	900	1125	1125	1375	1125	1375	1125	1375	1375	1600

*Scorch Recipe for Enjay Butyl 218

Polymer	100
Zinc oxide	2
Sulfur	2
Tetramethylthiuram disulfide	0.6

Scorch time	Min.	Max.
Minutes at 293° F	6	17

Base Recipe for Physical Properties

Polymer	100
Channel black	50
Zinc oxide	5
Stearic acid	3
Sulfur	2
Benzothiazolyl disulfide	0.5
Tetramethylthiuram disulfide	1

[a] Not a specification; values shown are typical. Method used for unsaturation was that of Rehner and Gray.

weight polymers would show curves very similar in shape to that of 215 but with some general flattening plus an extension of the "tail" in the high molecular weight fractions. In the case of these polymers, the amount of material falling into the higher fractions can begin to exert an appreciable effect on rheological processes.

Three additional butyl polymers which can be considered members of the same class but in a higher molecular weight range have been made available in limited quantities for experimental study. They have been designated ENJ-B-7, -8 and -6 and have viscosity average molecular weight of about 600,000, 850,000 and 1,200,000. Their molecular weight distribution plots would show

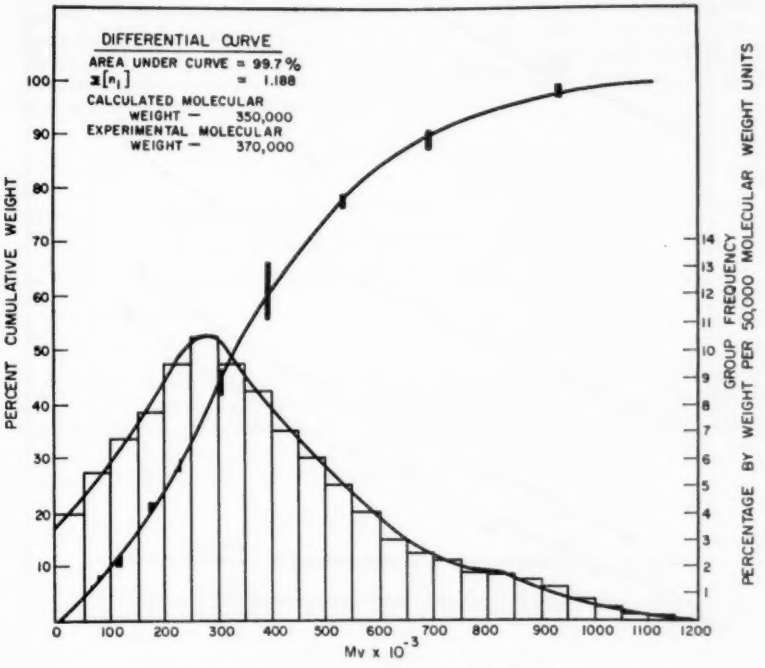

DIFFERENTIAL CURVE
AREA UNDER CURVE = 99.7%
Σ[η_i] = 1.188
CALCULATED MOLECULAR WEIGHT — 350,000
EXPERIMENTAL MOLECULAR WEIGHT — 370,000
PERCENT CUMULATIVE WEIGHT
GROUP FREQUENCY
PERCENTAGE BY WEIGHT PER 50,000 MOLECULAR WEIGHT UNITS
Mv x 10^-3
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
10 20 30 40 50 60 70 80 90 100
1 2 3 4 5 6 7 8 9 10 11 12 13 14

FIG. 1.—Molecular weight distribution of Enjay Butyl 215.

further "flattening" and extension of the high molecular weight species. As would be expected from the average, these polymers have relatively large amounts of polymer in the high fractions and this has a pronounced effect on rheological properties.

III. SIZE

Molecular weights and molecular weight determinations.—Due to the work of Flory, molecular weight determinations now rest on a rigorous thermodynamic basis. According to van't Hoff's law, the relation between the osmotic pres-

sure-concentration ratio of a substance and its molecular weight is

$$\pi/C \cong RT/M$$

At infinite dilutions this becomes

$$(\pi/C)_0 = RT/M$$

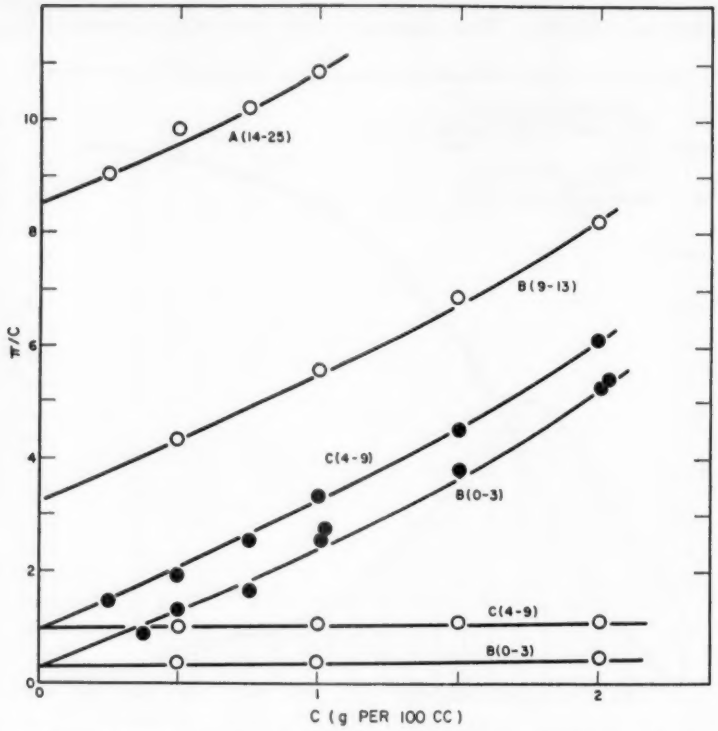


FIG. 2.—Osmotic pressure-concentration ratio versus concentration for polyisobutylene fractions in cyclohexane (●) and benzene (○) solutions (Flory[5]).

Flory[5] utilized the wide range of molecular sizes available through the fractionation of polyisobutylene to study molecular weight of polymers by osmometry. Thus, the link between classical methods of measuring molecular weight and the relatively intractable high molecular weight substances was achieved. The relationship between π/C and C for a number of polyisobutylene fractions in two solvents is shown in Figure 2. It will be observed that van't Hoff's law is obeyed but there is some deviation from ideal solution behavior. The difficulty of extrapolation through the resulting concave curves is reduced over that of the case of cyclohexane when the poorer solvent benzene is employed.

The coincidence of the $(\pi/C)_0$ points in the case of two fractions in the two different solvents attests to the legitimacy of the extrapolation procedure. Two choices are available for handling the extrapolation problem in osmotic pressure work. One has already been referred to in terms of the solvent in reference to the solvent-polymer interaction. The other is discussed by Flory[4b] and is based on a graphical method of Berglund. This method consists of plotting $(\pi/C)^{\frac{1}{2}}$ against C. The method yields linear plots. The graphical method ultimately provides a basis for computing $\bar{M}_n$. The method is only acceptable where π/C does not exceed 3 $(\pi/C)_0$.

The concept of the effect of a solute on the activity of a solvent in the osmotic pressure method is based on the number of solute particles present in the solution. Thus, the osmotic pressure method gives the number average molecular weight. The number average molecular weight is the true average of a heterogeneous polymer. The number average molecular weight counts each individual species of a given molecular weight and weights them according to their number present in the total number of molecules.

$$\bar{M}_n = \sum_1^\infty M_i N_i / \sum_1^\infty N_i + 1/\sum (X_i/M_i)$$

where M_i = molecular weight of species i

N_i = number of moles per gram of M_i

X_i = weight fraction of molecular weight

$X_i = N_i M_i$

$\sum X_i = 1$

The polyisobutylene fractions used in the osmotic pressure experiments were in turn used by Flory to determine intrinsic viscosity. The relation found for intrinsic viscosity and number average molecular weight is shown in Figure 3. The intrinsic viscosity determinations were made on diisobutylene solutions. The straight line is well described by the equation

$$\log M = 5.378 + 1.56 \log (\eta)$$

or

$$(\eta) = KM^a = (3.60 \times 10^{-4})(M^{0.64})$$

Because of its simplicity, the viscosity method is widely used. The molecular weight average it yields is not a true average. The method is based on the increased viscosity of solvents due to the perturbation effect of the polymer chains on the flow of the solvent. The effect of molecular weight on the viscosity of the solution is weighted in favor of the higher molecular weight species. The viscosity average molecular weight is given by

$$\bar{M}_v = (\sum M_i^a X_i)^{1/a} = \left(\frac{N_i M_i^{a+1}}{N_i M_i} \right)^{1/a}$$

As has been shown, the experimental parameter a is equal to 0.64. When $a = 1$, $\bar{M}_v$ is equal to the weight average molecular weight. This occurs when the molecular weight of the polymer is very low and the weighting factor towards the higher molecular weight species becomes negligible. This is shown by the convergence of the two curves in Figure 4 where $a = 1$ for the Staudinger

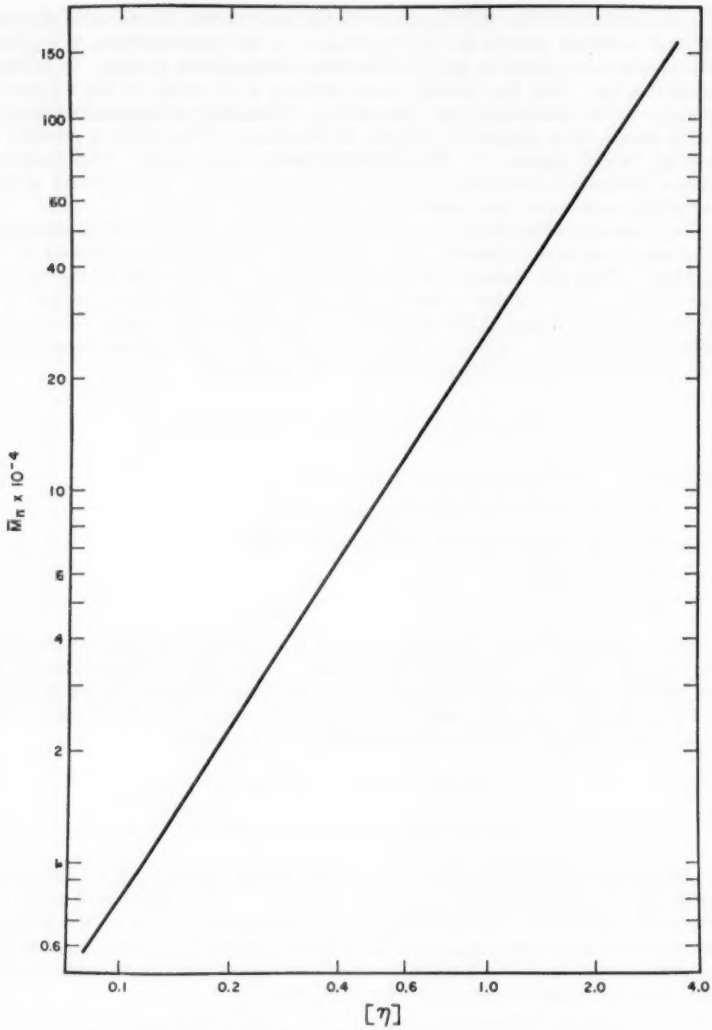


FIG. 3.—Relationship between log of number average molecular weight and intrinsic viscosity of polyisobutylene fractions (Flory[5]).

curve. Thus, the viscosity average molecular weight falls somewhere between weight average and number average molecular weight. For polyisobutylene, Rehner[6] has shown that

$$\bar{M}_v = 1.832\ (\bar{M}_n)(a = 0.64)$$

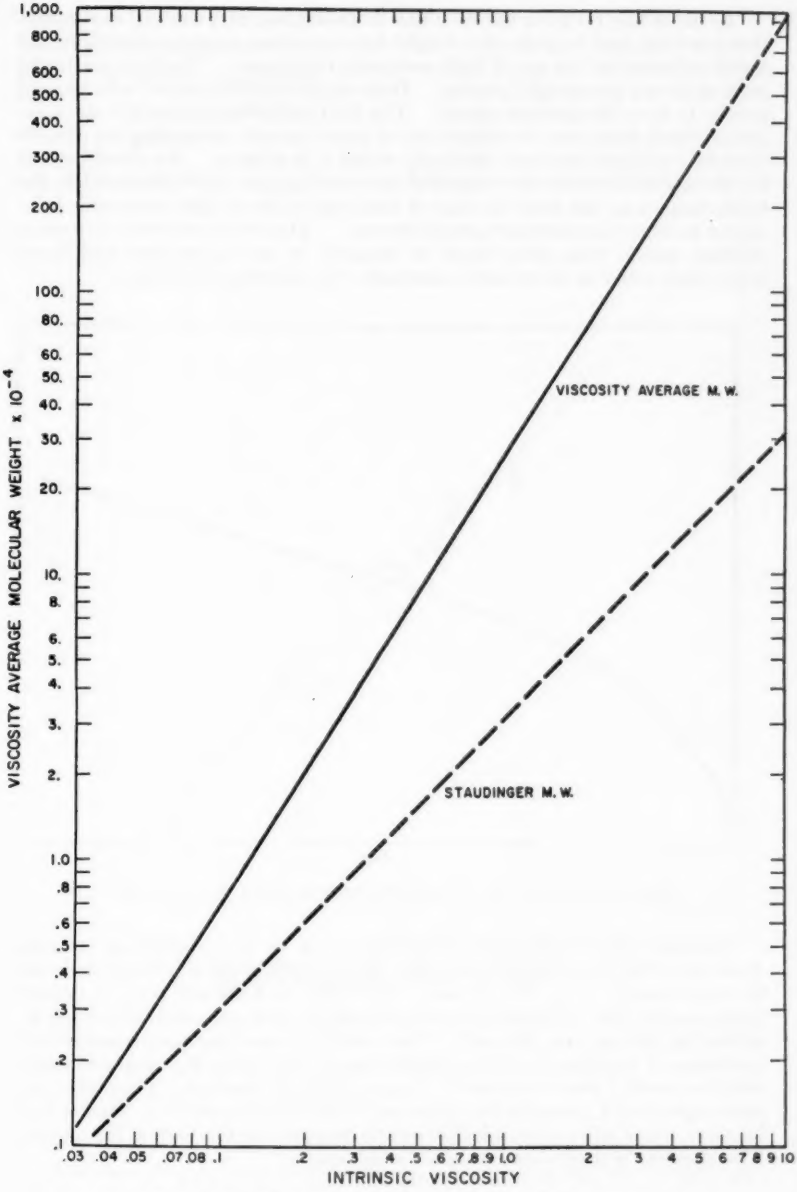


FIG. 4.—Viscosity average molecular weight versus intrinsic viscosity in diisobutylene at 20° C.

As far as this reviewer has been able to determine, very little, if any, attention has been paid to molecular weight determinations on polyisobutylene and butyl polymers by the use of light scattering techniques. The light scattering method gives a true weight average. However, it is not this aspect which would appear to have the greatest appeal. The light scattering dissymetry measurements which have been developed are of great value in measuring the dimensions of a polymer molecule randomly coiled in a solution. An elucidation of the structural effects in this type of chain would appear to be obtainable in the same manner as has been the case in the application of light scattering techniques to other polymers such as polystyrene[7]. The inferences relative to chain stiffness gained from other types of research on polyisobutylene and butyl copolymers could be made more quantitative by dissymmetry data.

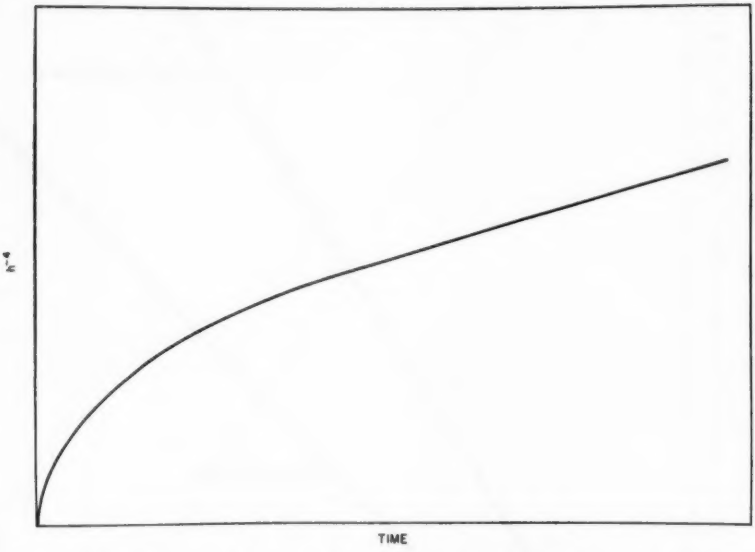


FIG. 5.—Typical flow curve for polymeric system in parallel plate plastometer.

Baldwin[8] carried out some interesting work on the relationship between molecular weight and polymer viscosity for unfractionated polyisobutylene and butyl polymers over a broad range of 300,000 to 4,000,000 using a parallel plate plastometer. The method and instrument used was essentially those described by Dienes and Klemm[9]. These authors based their work on Stefan's treatment of fluid flow between parallel plates. A typical flow curve obtained with the parallel plate plastometer is generalized in Figure 5. The plot of the plate separation h (actually the reciprocal of the fourth power of h) against time becomes linear after a short initial elastic response on the part of the sample. The viscosity is determined from the relationship.

$$h^{-4} = 8\pi Ft/3\eta v^2 + C$$

where h = distance between plates
F = applied force
v = volume of specimen
η = viscosity coefficient
t = time

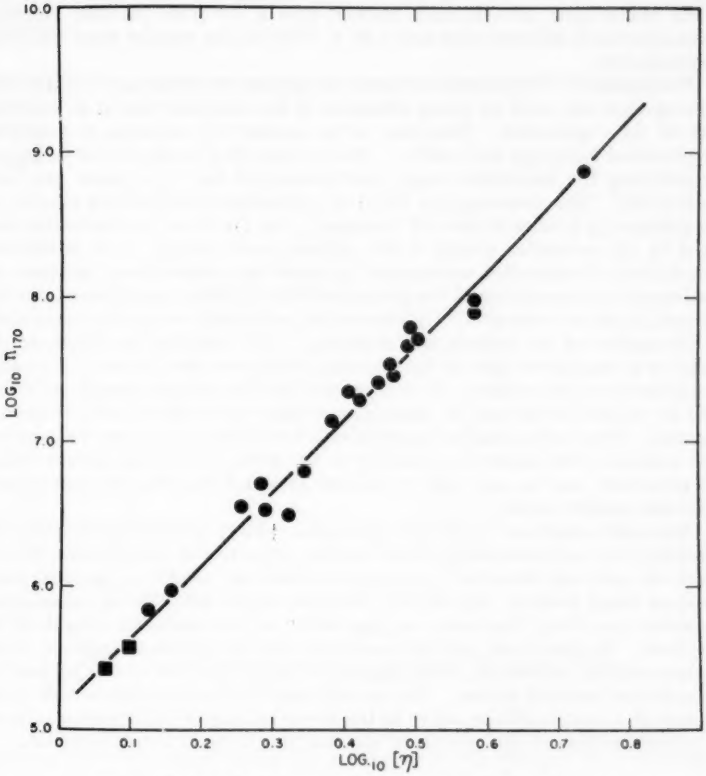


FIG. 6.—Relation between intrinsic viscosity and melt viscosity of butyl (■) and polyisobutylene polymers (●) (Baldwin[8]).

Baldwin's data on polyisobutylene and butyl polymers supplied a relationship between melt viscosity at 170° C and the intrinsic viscosity determined in diisobutylene solution. This relationship is shown in Figure 6. It was found that the relationship was represented by

$$\log \eta = A + B \log \bar{M}_w$$

The data obtained at a temperature of 170° C conformed to the equation

$$\log_{10}\eta_{170} = 5.120 + 4.725 \log_{10}(\eta)$$

A plot of $\log_{10}\eta_{170}$ against $\log_{10}(\eta)$ over a range of 0 to 0.8 shows excellent agreement. The constants derived by Baldwin from this melt viscosity method are slightly low and this is probably due to use of whole polymers and the subsequent heterogeneity. Nevertheless, this method has offered considerable advantage in molecular weight and rheological studies in these laboratories. The method was used to determine the viscosity average molecular weight of a polyisobutylene intended as a standard for dynamic testing[10]. A comparison of the values from two methods showed 1.35×10^6 from intrinsic viscosity measurements in diisobutylene and 1.48×10^6 from the parallel plate viscosity measurements.

Fractionation.—Preparation of close-cut polymer fractions can be extremely arduous when the need for sharp definition of the molecular size is an essential part of the experiment. However, for a number of purposes, a simplified fractionation technique may suffice. Such a simplified fractionation technique for studying the molecular weight distribution of butyl polymers has been worked out. The procedure for butyl or polyisobutylene involves solution of the polymer in a suitable solvent (benzene) at a given low concentration dictated by the molecular weight of the polymer under study. This is followed by addition of controlled incremental amounts of a nonsolvent (acetone) to portions of a given volume of the polymer solution. After equilibrated precipitations (about 48 hours at 30° C), the residual polymer in solution is determined by elimination of the solvent and weighing. This provides by difference the basis for a cumulative plot of the amount of polymer precipitated by a range of solvent-nonsolvent ratios. It is necessary that the solvent-nonsolvent ratios used be related previously to molecular weight fractions insoluble in such a mixture. Once such a relation is established for a polymer system of characteristic behavior with respect to solubility in the given solvent-nonsolvent ratios, the procedure can be used with confidence for most experiments over a wide molecular weight range.

Molecular weight and mechanical properties.—Flory[11], in a fundamental contribution to an understanding of the tension properties of vulcanizates, related effects of molecular structure (particularly molecular weight) to physical properties of butyl rubber. He showed that the tensile strength of vulcanizates prepared from butyl fractions was dependent on the molecular weight of the fractions. He postulated and demonstrated that the tensile strength of a vulcanizate should increase in linear manner with the fraction of the polymer in the principal network chains. The work is based on the fact that not all of the volume of a sample will be active in the stress-bearing or deformation process. A certain fraction of the volume of the sample will be in terminal chains.

$$\% \text{ terminal chains} = 100 \times (2/M)/(1/M_c)$$
$$= 100 \times 2M_c/(M + M_c)$$

where M = molecular weight of polymer before crosslinking

M_c = molecular weight of crosslink chain (number average)

when $M \gg M_c$

$$\% \text{ terminal chains} \cong 100 \times (2M_c/M)$$

The diolefin units in a butyl copolymer are believed to be distributed randomly along the polymer chains and crosslinking will also very likely show a

similar randomness. It will be noted that there will be two terminal chains for every primary molecule.

The tensile strengths of pure gum vulcanizates from a number of butyl polymer fractions are plotted against molecular weight of the fractions in Figure 7. It is immediately apparent that there is a range of low molecular weight polymers which are incapable of being crosslinked into a structure of reasonable mechanical strength. It can be inferred further that those parts of the network containing chains in the same size range will not be "active" in the stress-bearing network.

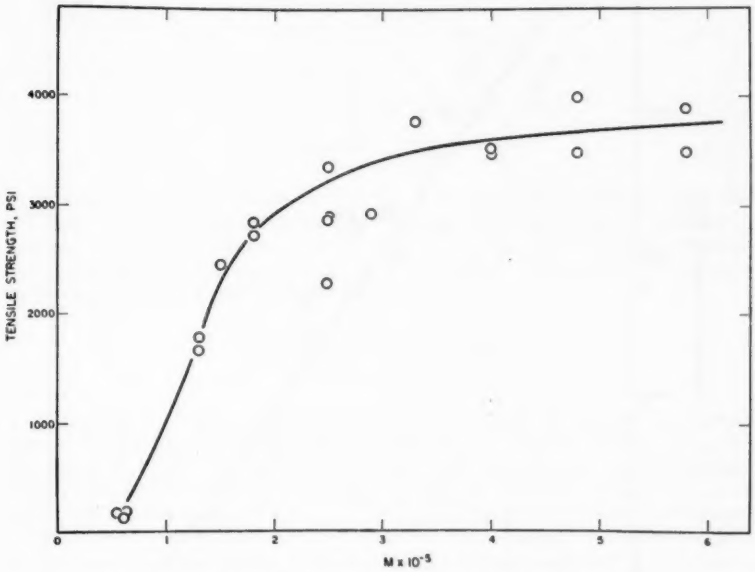


FIG. 7.—Tensile strength of pure gum vulcanizates of butyl polymer fractions as a function of molecular weight (Flory[11]).

The fraction of the vulcanizate occurring in principal network chains, exclusive of terminal chains which are not permanently oriented by stretching is given by

$$W_a = 1 - 2\,M_c/(M + M_c)$$

For a heterogeneous polymer, M would be replaced by $\bar{M}_n$. Thus, the tensile strength dependency on the fraction of the polymer involved in the orientation of stretching should increase linearly with $1/(M_n + M_c)$. The relationship found for the tensile strength of pure gum vulcanizates of a number of butyl polymer fractions on this basis is shown in Figure 8. Considering the nature of rupture phenomena and the experimental difficulty of eliminating scatter of tensile strength data on pure gum vulcanizates, the agreement with the predictions is amazingly good.

This work succeeded in placing tensile strength considerations upon sound theoretical grounds. In addition, the development of this dependence of a mechanical property on the "efficiency" of the crosslinked network has many technological facets. Any process which allows M_c to increase materially or which prevents the initial attainment of a reasonably low M_c will affect the stress-bearing properties of the vulcanizates. Low states of vulcanization,

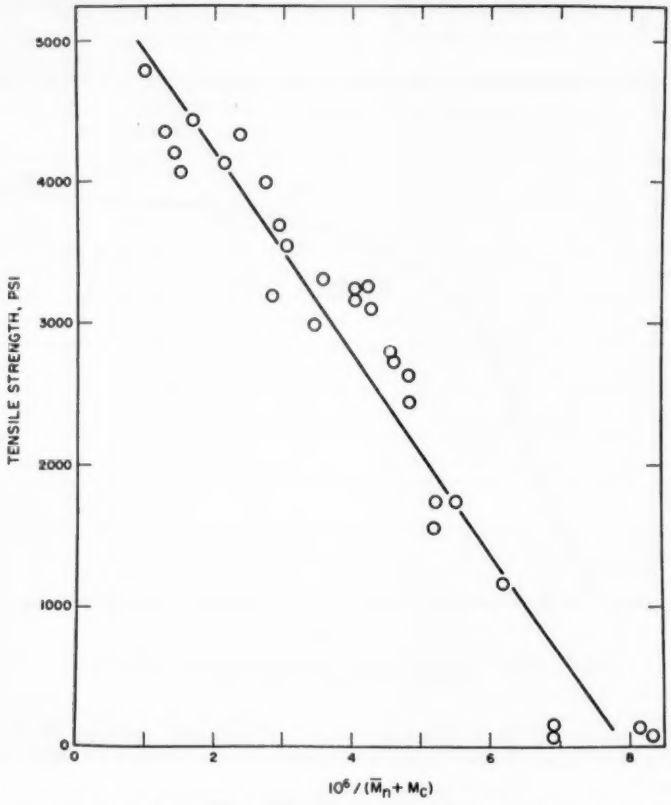
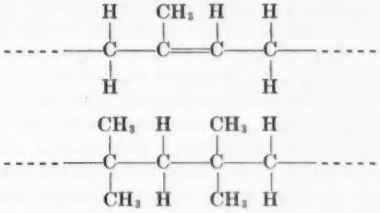


FIG. 8.—Tensile strength of pure gum vulcanizates as a function of polymer in active network. Vulcanizates derived from polymer fractions and mixtures thereof (Flory[11]).

dilution of the polymer with plasticizers, chain scission in reversion and oxidative reactions will all decrease tensile strength by reducing the amount of the polymer in the active principal network. It is apparent that the same effects will be observed in other mechanical properties of vulcanizates not involving catastrophe to the specimen. Flory observed that a similar dependence exists for creep. Other work in these laboratories support this view for practically any property of butyl vulcanizates involving deformation.

This relationship gives a clear picture of the effect of volume of polymer sample which is not included in the network and contributes little to the tension or other mechanical properties. An extension of this concept concerns the volume of the polymer sample *not* in the chain skeleton of the principal chains, such as side groups. This is an important consideration relative to butyl and other "branched chain" polymers. The relation of this to natural rubber is shown as follows for a 4-carbon unit in the polyisobutylene portion of the butyl chain.



If a C—C bond is considered as the unit involved in rupture, then the efficiency of the network in providing stress bearing chains can be evaluated in relation to "unused" polymer volume in methyl group or side chains. Assume equivalent volumes for equivalent polymer weights. Thus, the volume ratio for these comparable chain units would be

$$R_v = \frac{M_{\text{hevea}}}{M_{\text{butyl}}} = \frac{68}{112} = 0.61$$

Thus, natural rubber would have about 0.39 higher fraction of the sample volume functioning in a stress-bearing capacity. A similar anology could be developed for SBR. If this argument has merit, then the low tensile strength of polybutadiene should be explainable in part in terms of a large amount of chain volume not entering into the stress-bearing function because they are wasted in side groups in the form of short chains. Rehner[12] developed a relation between compressibility data and the known structures of polyisoprene, poly(dimethylbutadiene) and polyisobutylene that showed an inverse linear dependence on the number of side groups per C atom in the order given. It would be of interest to determine if polybutadiene fits into this relationship.

This line of thought on the efficiency of the stress bearing capacity of the chain and role of side groups in tension processes would appear very important. It would be of interest, for example, to examine the treatment of Bueche[13] of the ultimate properties for simple elastomers as it applies to a polymer such as butyl. Bueche's excellent treatment of this subject is based essentially on the calculation of the rate of disappearance of bonds in the network plane through which the applied tension is acting. The free energy change involved in the deformation process is developed on the basis of the change in configurational entropy. A constant term for the flexibility of the polymer chain is an essential part of Bueche's development. Thus, it would be of importance to consider whether the known difference in flexibility of the butyl chain as compared to other elastomers has a major bearing on the ultimate tension or elongation. It is important in work of this type to assure that the stress-strain relationship be as free of viscous effects as possible.

Molecular weight and rheology.—Zapp and Baldwin[14] related polymolecularity for butyl rubbers to viscoelastic processes particularly with regard to applicational rheology. Fractions of a butyl polymer were prepared and then blended back together to give four polymers of equivalent average molecular weight. Moreover, the blending scheme was designed to prepare polymers with molecular weight distribution extremes of 250,000 to 330,000 at the narrow end of the range and 20,000 to 1,000,000 at the broad end of the range. The viscoelastic properties of the polymers were studied in a number of deformation tests over a range of temperatures. These authors observed that in deformations at constant rate, the polymer of narrow molecular weight distribution was the most thermoplastic. The narrow molecular weight polymer also yielded a greater decrease in elasticity with increased temperature. Under conditions of constant load at 40° C, the viscous component of deformation (controlled by the average molecular weight which was constant) displayed by the several polymers was quite similar but the high elastic deformation was dependent on the distribution. The percentage of the total deformation due to the high elastic component was much greater for the broad molecular weight polymer. Increasing the spread of molecular weight for a polymer of given average molecular weight thus yields a softer, more elastic polymer. The practical relation of these observations on polymolecularity to millability and swelling on extrusion were considered.

TABLE II

TACK STRENGTH OF SEVERAL ELASTOMERS (FORBES AND MCLEOD[15])

Polymer	Raw tensile strength, psi	Tack strength, psi	Relative tack
Natural rubber	63.5	33.6	0.53
SBR	35.2	30.8	0.87
Butyl	50	46	0.91

Molecular weight, diffusion and adhesion.—Forbes and McLeod[15] presented information on the dependence of tack strength on molecular properties. This careful and extended treatment is believed to be the first comprehensive attempt at establishing such a relationship. Comparisons of tack properties, in the main, were between natural rubber, butadiene-styrene copolymers and butyl. A quantitative method was developed by these authors to give the force necessary to overcome the adhesion at two relatively fresh smooth polymer surfaces. Some comparative values for these polymers at approximately similar Mooney viscosities are shown in Table II. In contrast to feelings based on general practical experience butyl is found to have a higher tack strength than natural rubber. The level of tack strength for SBR is also higher than would be anticipated.

These authors found that the shear viscosity of these polymers was a major controlling factor in the relative tack values. A relation between relative tack values and the logarithm of the shear viscosity is shown in Figure 9. Despite differences in rate effects in both the tack and viscosity determinations (arising from the variety of polymers employed in the experiments), a fairly linear dependence is observed. This is in keeping with the thought that the adhesive strengths in polymers are dependent on diffusion of chains across an interface with the ideal being a complete obliteration of the interface. The goal would also entail having sufficently long chains involved in the diffusion process so that the adhesion strength would tend to approach the cohesive strength.

An extension of this line of thought to the adhesion between dissimilar polymers was made by these authors. In the case of dissimilar polymers, the nature of chemical differences in the polymers must be considered. This is necessary since the relative attraction or repulsion of the dissimilar polymer chains (sometimes referred to as mutual solubility or compatibility) would join with diffusivity in controlling the number of chains actually transported across the interface. These data for differences in solubility parameters, expressed as cohesive energy density for the polymer pair in question, are plotted relative to adhesion in Figure 10. The cohesive energy density values are originally attributable to Scott[16] and to Gee[17].

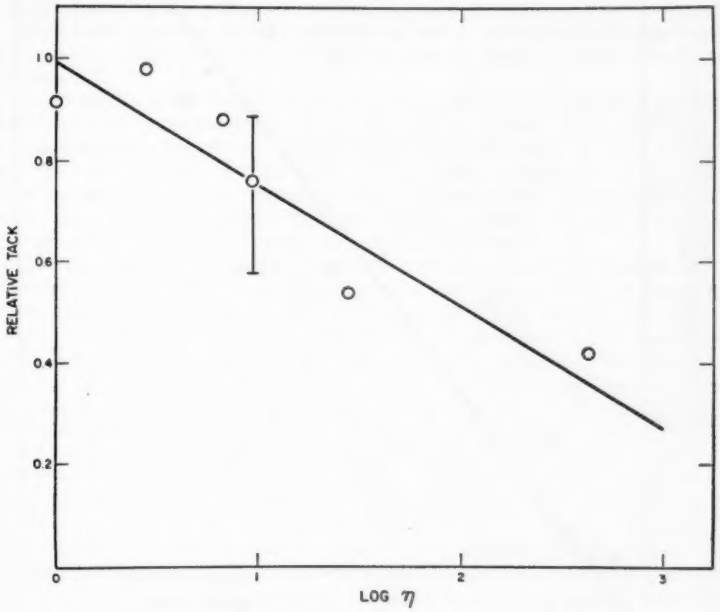


FIG. 9.—Effect of shear viscosity on relative tack (Forbes and McLeod[15]).

Considering the numerous factors which can affect this attempt at correlation, it must be admitted that the relation is very good. The general concept of transport of chains across an interface, together with favorable conditions from a mutual solubility standpoint as major factors in the process of securing adhesion seems very sound. Komskaya and Slonimskiĭ[18] concluded that most polymers can be mixed together to give a compatible system in a macro sense. However, such a mixture could show a lack of mutual solubility in microregions because of structural differences. Shapovalova, Voyutskiĭ and Pisarenko[19] concluded that temperature and time effects were important in that they facilitated diffusion of material at the interface. The present reviewer would like to extend this line of thought to the achievement of a strong bond at the inter-

face of a vulcanizate of two polymer layers in contact with each other. This postulate states that three factors are of primary importance in such a bonding system: (1) diffusion of chains in sufficient numbers across the interface and to sufficient depth below the interface, (2) similar chain flexibility and thus microcompatibility, and (3) mutual crosslinking processes for the reactive sites in the two polymers. General evidence for this postulate may be given as follows. Given sufficient time, application of heat and pressure, it would appear that

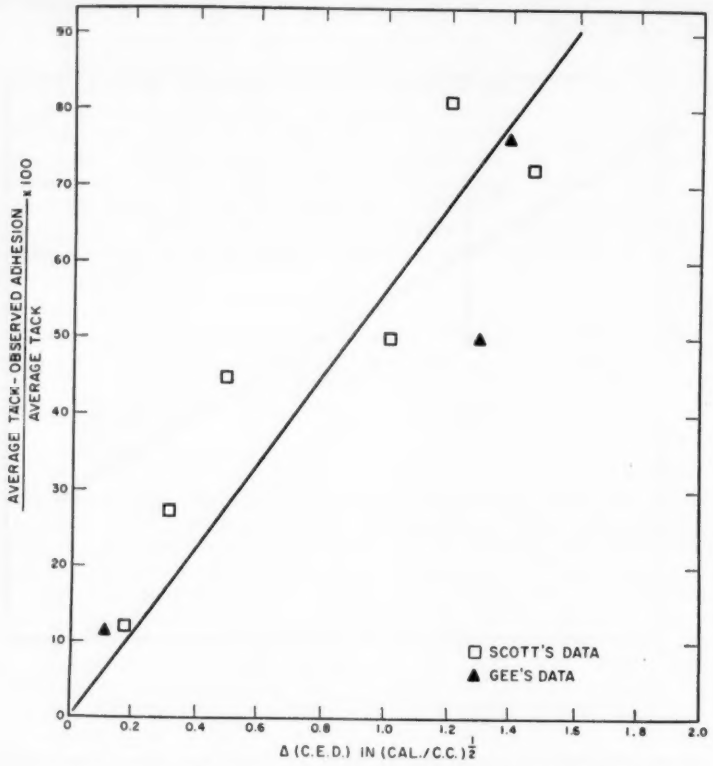


FIG. 10.—Effect of solubility parameter on adhesive strength (Forbes and McLeod[15]).

two polymers such as natural rubber and butyl would interdiffuse to a reasonable degree. This statement is strengthened by the small difference in the cohesive energy densities with natural rubber at 8.0 and butyl at ~7.8. However, long experience has shown that a satisfactory bond could not be achieved. Now with the advent of halogen (chlorine and bromine) containing copolymers of isobutylene and isoprene, satisfactory bonds are being achieved between natural rubber and these polymers. The new halogen containing polymers represent different crosslinking processes than is the case with butyl and these

probably provide a closer approximation of the necessary covulcanization of the present hypothesis.

Beckwith and associates[20] had previously arrived at a number of similar conclusions relative to the property of tack in butyl and natural rubber. They too associated the force needed to separate an interface (tack strength) with the force needed to break a specimen without an interface (stock strength). Their work also introduced a factor of the temperature of the knife (76° F versus 425° F to simulate the hot cutting blades of automatic inner tube splicing machines). Natural rubber compositions profited in higher tack strengths when the surfaces forming the interface were cut with the hot knife while butyl suffered in this regard. This could possibly be due to the rigosity of the surface brought about by the differences in rheological behavior of the two polymers. Contact time appeared to help natural rubber in attainment of higher tack whereas extended contact time did little to improve the tack of the butyl composition.

Prescorching of the butyl compositions had little effect on the tack strength and this is interpreted as being due to a favorable cohesive effect balancing an unfavorable adhesive effect. Carbon black decreased both the stock strength and the tack strength as a function of increasing particle size of the black. Since the ratio of the tack strength to the stock strength was reasonably constant, these authors concluded that the type of carbon black affects the tack strength only insofar as it changes the raw stock strength.

The importance of the adhesion of polymeric materials to themselves and to other forms of substrates is predominant in a very large number of uses. Because of this, a need for generalized knowledge in this field is now acute because of the many different polymers available and their combinations in adhesion systems with other materials. The relation of molecular size to attainment of adhesion strength is indicated in the dependence of this property on shear viscosity as noted earlier in this review. This dependence of the strength of the bond at the interface on the size of the molecules involved (shear viscosity) is in keeping with the observation of Bueche, Cushin and Debye[21]. These investigators found, in a study of selfdiffusion in solid polymers, that the log of the molecular diffusion constant for poly(*n*-butyl acrylate) is linearly related to the log of the viscosity and also linearly related to reciprocal temperature. These authors clearly recognized a number of experimental limitations particularly with respect to the molecular weight and temperature ranges in which their treatment would be applicable. However, it would appear from their work that selfdiffusion in solid polymers would conform to the following relationship.

$$D\eta = (ApkT/36)(R^2/M)$$

where D = molecular diffusion constant

η = bulk viscosity

p = density of polymer in sample

A = Avogadro's number

k = Boltzmann's constant

M = molecular weight

R^2 = average square end to end distance of a single polymer chain

This relationship, discussed by Bueche[22], is the product of an expression of Debye for free draining calculation of viscosity giving the bulk viscosity

$$\eta = \frac{R^2}{M}\frac{NpA}{36}f$$

and the relation of the molecular diffusion constant to the molecular friction constant

$$D = kT/\text{molecular friction constant}$$
$$= kT/Nf$$

where N = number of chain segments per molecule

f = friction constant

The importance of the problem of adhesion of butyl to other materials, particularly dissimilar polymers is well known. At least one of the major controlling factors, transport of material across the interface would now appear to be capable of study on the firm basis discussed here. Moreover, it is now recognized that polymer diffusion is operative in practically all of the processes involved in the use or adaptation of high molecular weight materials.

IV. SHAPE

The detailed properties of high polymers are controlled in a major way by the monomers in the chain and their arrangement and the resultant effects on what may be called the shape of the molecule. Many of the properties of butyl polymers are dependent on the isobutylene monomer which makes up the predominant part of the chain structure. For this reason, it is instructive to consider the research carried out on the structure of polyisobutylene since this will in the main be applicable to the predominant structure in the copolymer.

The helical structure for polyisobutylene.—Bawn[23] likens the structure of polyisobutylene to that of polyvinylidene chloride with the chlorine atoms replaced by methyl groups. A suggested chain configuration for polyisobutylene is shown in Figure 11. A distinct problem arose in attempting to fit the chain configuration to the fiber period obtained by x-ray methods. This was shown to be 18.64 A and containing eight monomer units repeating in that length.

Brill and Halle[24] found that when polyisobutylene is stretched it gives an x-ray fiber period quite similar to that of natural rubber. The fiber period observed in this work was 18.5 A. They postulated that this polymer has a helical chain structure rather than the zig-zag type common to paraffinic hydrocarbons and many other high molecular weight substances. Fuller[25] found similar evidence for a helical chain configuration. This was confirmed in joint work with Frosch and Pape[26]. In addition to the conclusion on helical form, it was observed that the chain molecules in the stretched polymer possessed a 1:3 disposition of the methyl groups.

The dimensions of the orthorhombic cell in crystalline polyisobutylene were found to be a = 6.94 A, b = 11.96 A, c = 18.63 A. The repeat distance of a specific arrangement of monomer units in the chain was thus found to be 18.63A in very good agreement with the observation of Brill and Halle. It was indicated in this work that the methyl groups are spaced 2.33 A apart along the fiber direction. This is the basis for eight monomer units in the fiber period.

Construction of a scale model on the basis of 1:3 arrangement of methyl groups brings out another important aspect relative to these side groups. In order to comply with the tight packing in this chain structure, it is necessary that the line joining the carbon atoms of each methyl group pair form an angle of approximately 22.5° with the plane perpendicular to the molecule axis. From these considerations, a chain structure of eight monomer units with staggered methyl groups achieving one complete revolution about the chain axis in the fiber period distance was evolved.

The head-to-tail structure.—Although Astbury[27] and later Bunn[28] did not agree with these views, it should be noted that their suggested models also involved rotation of the monomer units to give spiral forms. It would appear that the concept of the tight "wound-up" structure for the polyisobutylene chain has considerable merit and this has profound bearing on the properties of this polymer and its copolymer with minor amounts of diolefin. The numerous

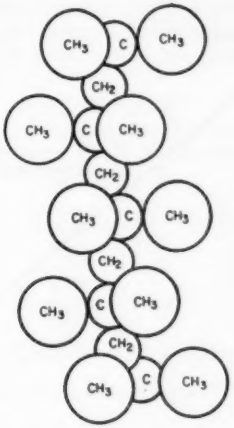


FIG. 11.—Suggested chain configuration for polyisobutylene (Bawn[28]).

effects of the tightly spaced large methyl groups can be readily visualized from these considerations.

It is of interest that one of the major considerations in Bunn's departure from the suggested structure of Fuller et al. related to the matter of consistency of head-to-tail monomer arrangement. His argument pertained to the fact that it is not known with certainty that the polymer is completely a head-to-tail structure. Although it would appear that this polymer is predominately the head-to-tail structure, it must be admitted that there is no experimental proof that it is completely so. The amount of other monomer arrangements which would be present in polyisobutylene and butyl may not affect the general conclusions of Fuller. However, the presence of small amounts of other structures distributed at random throughout the head-to-tail structure could be of importance. This point will be referred to later in this review.

Relation of structure to polymer properties.—In view of the crowded structure, it is not surprising that the polyisobutylene and butyl chains, although composed almost entirely of single carbon to carbon bonds, except for termini,

should have less flexibility than normal. From the structure shown in Figure 11, it is easy to see how the presence of two methyl groups on one carbon atom leads to considerable steric hindrance to rotational freedom. Rehner noted in a study of the compressibility of rubbers that the presence of methyl side groups decreased the compressibility. His data are shown in Figure 12. It may be noted that as methyl substitution along the chain is increased, the compressibility decreases for the polymers, polyisoprene (natural rubber), polydimethylbutadiene and polyisobutylene. Rehner related the repulsion between the substituent groups to freedom of rotation or flexibility.

It is of interest to note that a polar group such as the nitrile of Hycar OR has an effect on compressibility equivalent to the one methyl group per chain

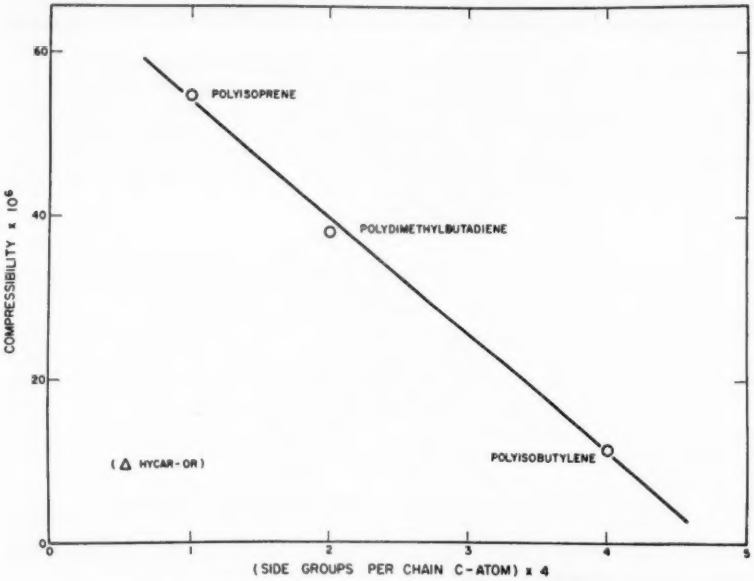


FIG. 12.—Effect of chemical structure on compressibility (Rehner[12]).

carbon atom of polyisobutylene. Rehner used Hycar OR-15 in his work. If we assume, for the purpose of rough calculation, that this polymer contained a 65–35 ratio by weight of butadiene and acrylonitrile in the average chain, we obtain one nitrile group for about every nine carbon atoms in the chain. The nitrile group can be considered to have about the same size as the methyl group. In this sense, the effect of the polar group is larger than would be expected. Possible explanations of this phenomenon may be that the butadiene monomer units have given rise to small branches with the effect similar to a methyl group or that interchain and intrachain interactions are operative to reduce the compressibility. It would be of interest in view of this to obtain compressibility data on polybutadiene from normal emulsion polymerization and *cis*-polybutadiene now available from newer polymerization systems.

Permeability to gases and structure.—Amerongen[29] found that molecular structure of polymers is the dominant factor in controlling permeability to gases. In general, structures which allow considerable chain freedom as a class also allow higher permeabilities. Since for given gases the solubilities do not differ very much, it must be concluded that the structures exert their major effect on the diffusion of the gas. This may be considered simply as the presentation of the longest free path to the diffusing gas molecule. This concept, in turn, can be considered in terms of the number and size of "holes" which open up in the polymer membrane during any given interval of time during the permeation measurement. Conceivably, such a thought could be developed to appraise the size of the segmental unit involved in chain motion and the degree of chain cooperation needed to allow gas molecules to diffuse at a given rate.

Some of Amerongen's data for permeability, diffusivity and solubility of nitrogen in various elastomers at 25° C are shown in Table III. In general, it can be seen that the polymers line up in the proper order which might be expected from the broad knowledge of flexibility of these polymers which has been obtained to date. It is seen that the chain flexibility associated with

TABLE III

PERMEABILITY AND DIFFUSIVITY OF NITROGEN IN VARIOUS ELASTOMERS AT 25° C (AMERONGEN[29])

Polymer	Permeability[a]	Diffusivity[b]	Solubility[c]
Natural rubber	6.6×10^{-8}	11.5×10^{-7}	0.056
Buna-S	4.8	10.0	0.048
Perbunan	0.89	2.3	0.038
Neoprene G	0.89	2.4	0.036
Oppanol-B-200	0.22	0.43	0.049
Butadiene rubber	4.9	11.0	0.045
Methyl rubber	0.36	0.79	0.045

[a] Cc of gas (0° C and 760 mm Hg) penetrating 1 sq cm surface of sample 1 cm thick per second at 1 atmosphere gas pressure.
[b] Sq cm per second.
[c] Cc of gas (0° C and 760 mm Hg) dissolved per cc of elastomer at 1 atmosphere gas pressure.

natural rubber, Buna-S and butadiene rubber gives rise to permeability values much higher than those obtained for the "hindered" structures of the polar and high methyl side group polymers. Since, for nitrogen, the solubilities do not change very much, it follows that the diffusivity of the nitrogen gas molecules in the polymer determines the amount of gas transported through the membrane.

Diffusivity and mechanical properties.—Auerbach and associates[30] reported on the use of a diffusivity approach for studying polymer structure. The diffusivity of a number of compounds in the C_{18} range prepared with C-14 was studied for a variety of polymer types. These investigators reasoned that research on the diffusion of small "polymer" molecules in a macromolecular medium could lead to a better understanding of the form, flexibility and composition of the chain molecules. This work may very well be the beginning of a detailed experimental insight into a field where fundamental theory has yet to be developed.

One of the several applications of this approach concerned the relation between energy losses (arising from internal friction) and temperature. A plot of these relations for a number of polymers showing different diffusivities is shown in Figure 13. This plot was an effort to describe the size of the chain

unit involved in the deformation process in relation to the size of a diffusing molecule such as octadecane. The fact that there is some relation between the diffusivities of octadecene in the four polymer types and the internal friction at low temperature is a very hopeful sign. Here, the diffusivities for polyisobutylene, polyisoprene (emulsion), polybutadiene and natural rubber begin to line up in the proper reverse order with the internal friction values. It thus would not appear unreasonable to expect that when the two properties are compared at the proper temperatures and over a range of frequencies, a more general relationship may be obtained.

Structure of diolefin units in the polymer chain.—The combined results of the work of Thomas and associates[31] and Fuller, Frosch and Pape have established that the predominant part of the polyisobutylene chain has the head-to-tail

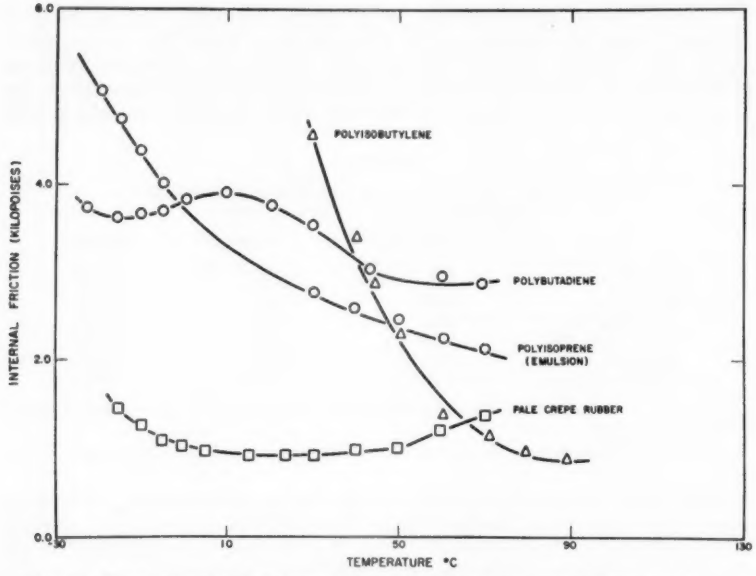
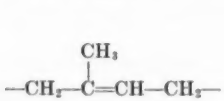
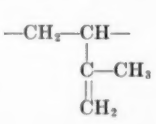


FIG. 13.—Plot of internal friction observed in dynamic tests at 60 cps. versus temperature for some of the elastomers used in diffusivity studies (Auerbach[30]).

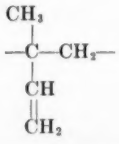
structure shown previously in this review. Similarity in x-ray diagrams for polyisobutylene and the copolymer with isoprene allow the conclusion that a similar structure can represent the butyl chain. Rehner[32] considered the detailed structure with respect to the copolymer and the manner of entrance of the diolefin isoprene into the chain. Three possible structures were considered.



Structure I



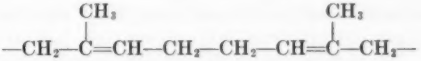
Structure II



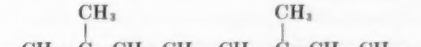
Structure III

The problem of definition of which structure best represents the diolefin units in butyl was attacked by a method employing double bond cleavage with ozone. It was reasoned that ozonolysis of Structure I would lead to only aldehydes or acids having (2n + 4) chain carbon atoms. Formaldehyde or formic acid derived from terminal double bonds was discounted on the basis of the minute amount of aldehyde or acid arising in this way in a polymer of high molecular weight. Ozonolysis of Structures II and III would yield one molecule of either formaldehyde or formic acid for each side-chain methylene group. Thus, the presence of Structure I and Structures II and III could be defined. No distinction relative to Structures II and III could be made, however. The formaldehyde and formic acid from Structures II and III would be present in water extracts of the ozonized polymer. None of either compound was found and Rehner concluded that the 1,4 addition of Structure I best represents the diolefin structure in butyl.

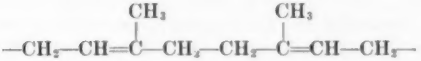
A further consideration of the structure of butyl concerns the possibility of sequences of diolefin units in the polymer molecule. If random entry of the isoprene in the chain did not occur then a number of groupings are possible.

I. 

Tail-to-Tail Structure

II. 

Head-to-Tail Structure

III. 

Head-to-Head Structure

Ozonolysis of Structure I should yield succinaldehyde or succinic acid; Structure II levulinic aldehyde or levulinic acid; Structure III acetonylacetone. No evidence could be detected in specific tests for the presence of any of the products associated with the sequential structures shown. It was thus concluded that the isoprene units entered the chain as single molecules.

Although the predominant structural features of the butyl chain seem to have been well established, one point remains of considerable interest to this reviewer. This area of interest concerns the possibility of the occurrence of small amounts of isobutylene monomer entering the chain in other than head-to-tail structures. The type of work done to establish the structure of polyisobutylene does not preclude this possibility. Evans and Polyanyi calculated the heats of reaction for head-to-tail as 19.5 kcal, tail-to-tail 27 kcal and head-to-head 12 kcal per mole. The measured heat of polymerization is 12.8 kcal per mole. The difference between the heat for the head-to-tail reaction and the measured heat is ascribed to steric influences. However, it would appear from this that on an energy basis the head-to-head reaction is possible. The importance of this discussion is whether the existence of a small but significant number of head-to-head sequential arrangements, randomly distributed along the polymer molecule, could give rise to "weak linkages". Such weak linkages, if present, could be of considerable importance in the initiation of chemical deg-

radation of the chain in an oxidative process or bond rupture in a tension process such as dynamic fatigue or straining to maximum extensibility. It would appear that a careful pyrolysis experiment followed by complete spectroscopic examination of the products would be of value.

Order and disorder.—The terms order and disorder relative to polymer structure have taken on specific meanings since the advent and development of polycrystalline materials. However, the connotations assigned here to these terms relative to butyl polymers are somewhat different as will be apparent. Butyl polymers are normally completely amorphous when at rest. They can be readily brought into a crystalline state upon stretching. Under these conditions, they give x-ray diffraction patterns of exceeding sharpness and detail. It would be expected from this that spontaneous crystallization of butyl vulcanizates would occur quite readily under the proper conditions. However, efforts in these Laboratories to encourage crystallization at low temperatures were unsuccessful. Dilatometric techniques were used at a temperature of $-20°$ F over a period of 30 days[33]. However, Gehman and associates[34] found evidence of crystallization in butyl in a torsional measurement of stiffening. They used a temperature of $-57°$ C over about the same period of time. These findings were considered confirmed when they observed a sharpening of the rings in the x-ray pattern for a butyl vulcanizate held at low temperatures for a long period. More recently, Kell and associates[35] studied the crystallization of polyisobutylene and butyl polymers in the unstressed state and at temperatures ranging down to $-60°$ F for times up to 18 months. These investigators employed dilatometric techniques. Polyisobutylene crystallized readily in 5–10 days in the temperature range -25 to $-42°$ C. The maximum rate of crystallization appeared to occur at -33 °C. Crystallized samples returned to the amorphous state when the temperature was slowly raised to 0° C. Of the butyl polymers, only the one containing the lowest diolefin content (referred to as GR-I-35) crystallized. It required approximately one year and a temperature of $-30°$ C to achieve this state. The butyl polymers containing higher amounts of diolefin did not crystallize although held at the low temperatures for one and one-half years. The early lack of success in obtaining spontaneous crystallization in butyl polymers may be the result of one or more of the three following reasons: (1) lack of recognition of the preferred temperature for appreciable rate of crystal formation, (2) insufficient time of exposure to the low temperatures, and (3) a possible interference on the part of the diolefin with the perfection of chain alignment required for true crystallinity. It would be expected from the decrease in chain mobility of this polymer at low temperatures that the time to achieve crystallinity would be quite long.

Butyl polymers may be considered regular in certain major structural aspects and random in others. It has already been shown that the chain is composed mainly of head-to-tail monomer arrangements. Further, these monomers form a complete helix in the chain for every eight units present. Thus, the general order evidenced in the sharp x-ray diffraction patterns should not be unexpected. In a minor sense the butyl chain shows structural randomness inasmuch as the diolefin units are not regularly spaced. However, the diolefin units are shown to be regular as to their manner of entrance into the chain (1,4 addition) and the absence of any grouping of units. As would be expected from the foregoing discussion, branching is considered to be completely absent in the butyl polymers which have been produced commercially to date. This however is a function of the amount of diolefin used in the polymerization feed. It has been observed, in these Laboratories, that when the diolefin to

olefin ratio is increased materially in the butyl polymerization, highly gelled polymers result.

V. CHEMICAL COMPOSITION

General.—As has been shown, the term butyl represents a copolymer of an olefin and a multiolefin. The polymers which have reached commercial maturity are copolymers of isobutylene and isoprene. A descriptive list of these polymers in terms of molecular weight, Mooney viscosity and unsaturation has already been given. Other butyl polymers have been prepared on an experimental scale with some of the diolefins being butadiene, dimethylbutadiene, piperylene and cyclopentadiene. Tripolymers have been made commercially on a limited scale with divinylbenzene. Although each of these has its own set of interesting properties, they will not be considered here. This review concerns itself chiefly with the isobutylene-isoprene copolymer. One departure from this plan involves the halogen containing copolymers treated in another section.

Butyl can be crosslinked by virtue of the fact that the isoprene introduces allylic hydrogen atoms into the otherwise unreactive chain. It is believed that all crosslink junctures arise at these points during all types of crosslinking reactions.

The low concentration of double bonds in butyl is considered to be the reason for its high resistance to oxidizability in keeping with normal olefin chemistry. However, this point will be discussed further in this review. There appears little doubt that the low double bond concentration confers on butyl its resistance to attack by ozone since ozone rapidly cleaves such links. The large concentration of tertiary carbon atoms is an important factor in the general oxidation of hydrocarbon chains and this must be considered. It is known that there are large increases in oxidizability in going from primary to secondary and tertiary carbon atoms. Moreover, the methyl group is relatively easy to oxidize to a carbonyl and associative factors resulting from this may be important in the general problems of aging and stabilization. It is also conceivable that the bond strength of the carbon-carbon atoms can be an important consideration in rupture processes such as stretching to break, cracking, tearing and abrasion.

Importance of diolefin content and its measurement.—The most important point in the chemical composition of butyl is, of course, the concentration of diolefin which has entered the chain. It can be shown that small variations in the isoprene content of butyl can have marked effects in the vulcanization process and properties of resultant crosslinked networks. Moreover, many theoretical problems require an accurate knowledge of the absolute value of the unsaturation. The problem of the relative or absolute correctness of the measurement of isoprene or double bond concentration arises from the relatively small amount of diolefin in the chain. This problem has had, therefore, to be approached in a radically different manner than is the case with higher unsaturation polymers.

Halogen addition to olefinic linkages represents one of the first methods of measurement of unsaturation in butyl rubber. The classic iodine monochloride was used originally. An improved method, employing iodine in the presence of mercuric acetate and trichloroacetic acid, has been described by Gallo, Wiese and Nelson[36]. This is the standard method used in these Laboratories. In this method, a solution of the polymer in carbon tetrachloride is treated with iodine in the presence of mercuric acetate and trichloroacetic acid

for 30 minutes. Sodium thiosulfate is used to titrate the excess iodine. The iodine number is obtained as follows:

$$\text{Iodine Number} = \frac{\text{ml} \times N \text{ of } Na_2S_2O_3 \times 126.91 \times 100}{\text{grams of polymer} \times 1000}$$

The mole per cent unsaturation is obtained from the iodine number and molecular weight of the monomer (56.10 for isobutylene at low isoprene content) as follows:

$$\text{Mole per cent unsaturation} = \frac{M \text{ (iodine number)}}{126.91F}$$

Here F is a stoichiometric factor and for the reaction described has been taken as equal to 3. This reaction is usually described as "drastic". A moderate reaction, in the absence of trichloroacetic acid, has also been used.

Rehner[37] earlier had carried out a comprehensive study of reactions of nitrosobenzene, thiocyanogen, iodine monochloride and ozone with polyisobutylene and butyl polymers. Polyisobutylene was included to serve as a measure of the effect of terminal double bonds on the unsaturation values obtained. Rehner felt that the nitrosobenzene addition reaction is unsuitable for this purpose because of complications due to oxidation; incomplete reaction due to polymerization of thiocyanogen makes this reaction unacceptable; and finally, the halogen reaction was suspected of proceeding by both substitution and addition routes.

The ozonolysis method is based on degrading a solution of polymer to a limiting viscosity dependent on the number of double bonds in the original polymer chain. Thus, the limiting viscosity would be a measure of the mean size of the polymer existing between successive double bonds in the original polymer.

The method consists of degrading the polymer in solution of carbon tetrachloride by passing through an air stream containing about 0.25 volume per cent of ozone. The solution is maintained at 0° C during the degradation process. The passage of ozonized air is continued until the intrinsic viscosity of the polymer products is constant. Samples at various times are taken up in diisobutylene and their intrinsic viscosity determined at 20° C. Typical curves of intrinsic viscosity versus time of passage of air are shown in Figure 14. The ease of extrapolation to zero time of ozonization and the intrinsic viscosity of the polymer fragments is apparent in these plots.

In order to obtain the unsaturation value from the limiting viscosity, it is necessary to convert the viscosity average molecular weight derived therefrom to the number average molecular weight. After Flory, the viscosity average molecular weight for polyisobutylene is given by

$$\bar{M}_v = \left(\sum_i N_i M_i^{a+1} / \sum_i N_i M_i \right)^{1/a}$$

where $a = 0.64$ and N_i and M_i are the number and molecular weight of species i. Rehner gives the random cleavage as

$$N_i = N(1 - p)p^{i-1}$$

where p is the probability of cleavage. Substituting the right hand side of this expression in the Flory equation and changing the summation in the numerator to an integral gives the viscosity average molecular weight of the cleaved polymer fragments as

$$\bar{M}_v = \left[\int_0^\infty N(1-p)p^{i-1}(iM_0)^{a+1}\, di / \sum_i N(1-p)p^{i-1}iM_0 \right]^{1/a}$$

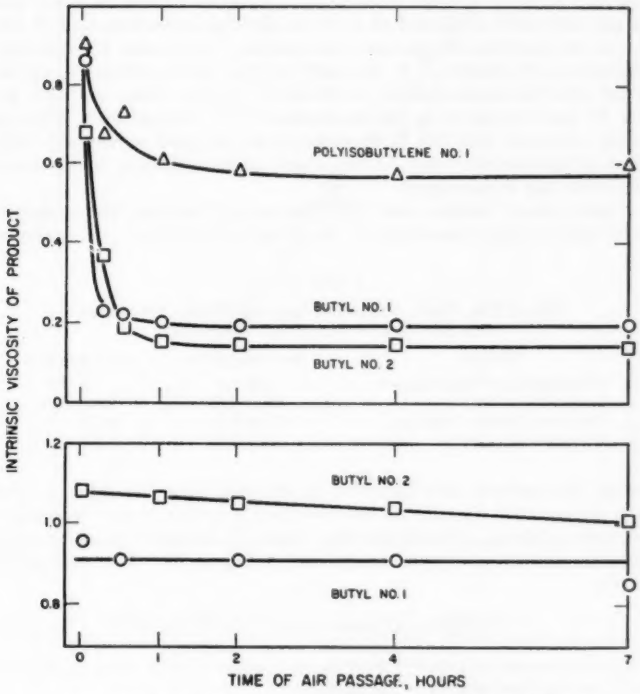


FIG. 14.—Rate of degradation of polyisobutylene and butyl rubber by ozone and by air (Rehner[32]).

where $M_i = iM_0$ and M_0 is the molecular weight of the monomer unit. Since the sum of the fragments resulting from cleavage is

$$\sum_i N(1-p)p^{i-1}\, iM_0 = M_0N/(1-p)$$

the viscosity average molecular weight is

$$\bar{M}_v = \left[(M/p)(1-p)^2 \int_0^\infty i^{a+1}p^i di \right]^{1/a} \cong [(1+a)\Gamma(1+a)]^{1/a}/(1-p)$$

Since the number average molecular weight is given by $\bar{M}_n = 1/(1 - p)$, then

$$\bar{M}_v/\bar{M}_n = [(1 + a)\Gamma(1 + a)]^{1/a} = 1.832$$

Thus, a conversion factor for changing the viscosity average molecular weight to the number average molecular weight for the polymer fragments from the ozonization process is found to be 1.832.

Rehner obtained independent confirmation of the unsaturation values from the ozonolysis experiment by two chemical methods. One method consisted of titrating the carboxyl groups formed by hydrolysis of the ozonized terminal groups and the other consisted of a micro-Kjeldahl determination of nitrogen content of the polymer fragments after forming hydrozone by reaction with 2,4-dinitrophenylhydrazine. A summary of the unsaturation values for two butyls (of different unsaturation) as obtained by these three methods is given in Table IV and compared to values obtained with concentrated Wijs reagent. It may be observed that the three methods are in good agreement with each other but all give unsaturation values which are considerably lower than those obtained with the Wijs reagent.

In a later paper, Rehner and Gray[38] developed further information on the details of experimental procedure in the ozonolysis method. A major simplification in the method was achieved in showing that the intrinsic viscosity could be determined directly on the ozonized polymer in the original carbon tetrachloride solution. Corresponding values of intrinsic viscosity in carbon tetrachloride and diisobutylene are shown in Figure 15. The proportionality is given by

TABLE IV

MOLE PER CENT UNSATURATION OF BUTYL POLYMERS BY DIFFERENT METHODS (REHNER[37])

Method	Butyl sample #1	Butyl sample #2
Concentrated Wijs reagent	0.8–1.1	1.7–2.0
Ozone-viscosity	0.51–0.57	0.80–0.86
Ozone-carboxyl titration	0.46–0.64	0.78–1.1
Ozone-hydrazone	0.52–0.69	0.88–0.96

$$K = [\eta]_{CCl_4}/[\eta]_{\text{diisobutylene}} = 1.255 \pm 0.005$$

Thus, the conversion to number average molecular weight relationship for solution in diisobutylene can be made readily.

An absolute method for measuring unsaturation in butyl.—McNall and Eby[39], prompted by the difference between the unsaturation values from ozonolysis and halogen reagent techniques, inquired into the possibility of an absolute measurement. They prepared butyl polymers with C-14 containing isoprene. Unsaturation values were obtained by drastic and moderate iodine-mercuric acetate methods and by ozonolysis. The comparative data obtained are shown in Table V for two butyl polymers of widely different isoprene content. It is evident that the halogen method approaches the absolute unsaturation much more closely than the ozonolysis method. This is particularly true when the stoichiometric factor is set at 2 instead of 3. These authors suggest a factor of 2.61. Thus, the mole per cent unsaturation on this basis would be given by:

$$\text{Mole per cent unsaturation} = 0.1694 \times \text{Iodine Number}$$

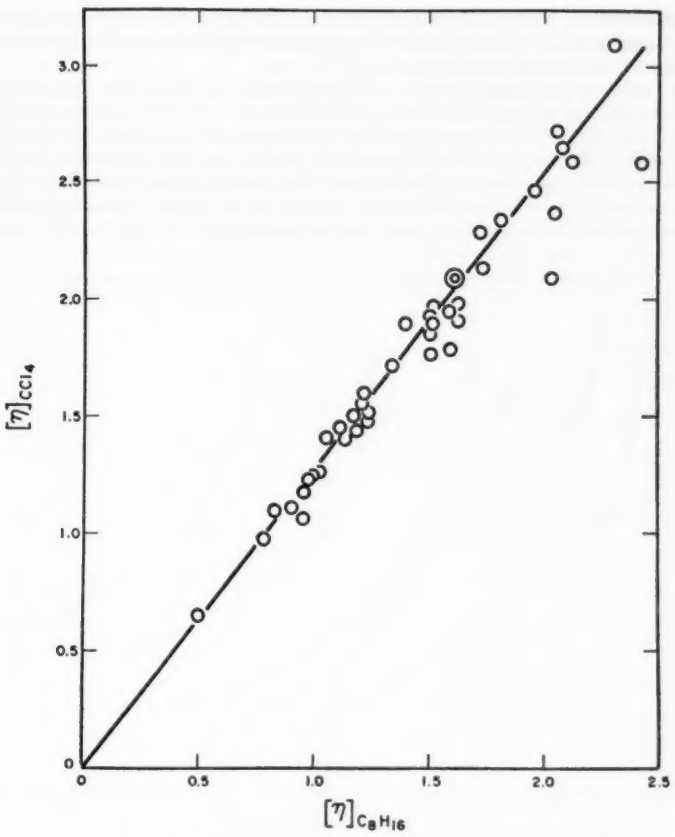


FIG. 15.—Corresponding values of intrinsic viscosity in carbon tetrachloride and in diisobutylene (Rehner and Gray[38]).

TABLE V

DETERMINATION OF ABSOLUTE UNSATURATION BY VARIOUS METHODS (MCNALL AND EBY[39])

Butyl sample	Unsaturation by C^{14}-Isoprene	Per cent of absolute unsaturation[a]				
		Iodine-mercuric acetate method				
			$F=3$		$F=2$,	
		Drastic	Moderate, 30 minutes	Moderate, 1 minute	Moderate, 1 minute	Ozone
B-3	1.23	86	78	70	104	57
B-15	5.71	88	73	65	98	33
		Av. 87	76	68	101	45

[a] Referred to unsaturation in C-14 isoprene analysis.

Attempts by these authors to develop a method based on infrared spectra were unsuccessful. The difficulties in such a method were ascribed to low absorption of the *tertiary* double bond.

An important anomoly.—In view of these further developments, it is of interest to reconsider the results of the work by Rehner. It would appear very unlikely that the excellent agreement of the unsaturation values for the three methods of Rehner could be fortuitous. However, the difference between Rehner's results and those of McNall and Eby would appear to be real. Thus, the cause of the differences must reside in the nature of the polymer fragments after degradation by ozone in a solution of carbon tetrachloride. This aspect

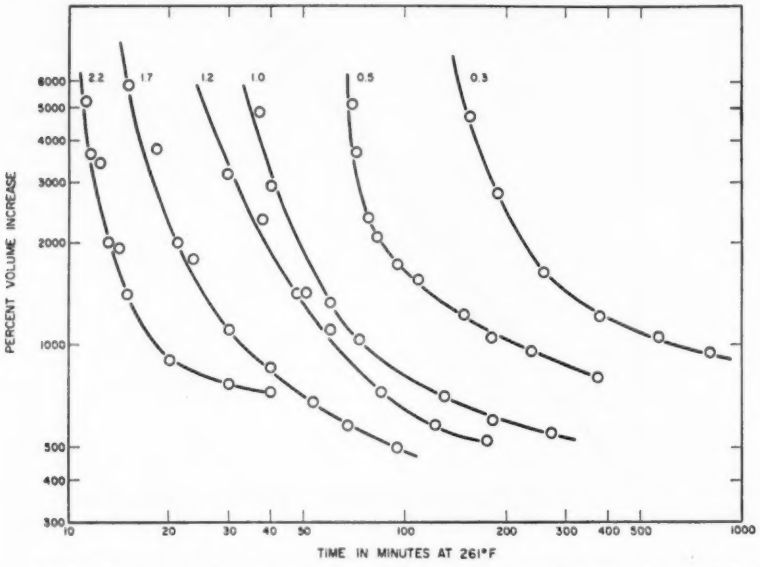


FIG. 16.—Volume swell in cyclohexane at 25° C with respect to vulcanization time for tetramethyl thiuram disulfide accelerated system. Curves are identified relative to mole percent unsaturation of polymer used (Zapp[46]).

of the methods of measuring unsaturation in butyl polymer requires clarification. The importance of this point relates to further progress in studying crosslinked structures of butyl. It has been observed that vulcanized butyl can be swollen in carbon tetrachloride and then degraded by ozone much in the manner developed by Rehner, as long as double bonds are still present. This would appear to be a powerful tool in studies of crosslinked networks. However, until the anomoly referred to is eliminated the use of this method to study polymer fragment size after ozonization of a swollen vulcanizate has limited value.

VI. CROSSLINKING

Low functionality concept.—Butyl introduced a new concept into the field of elastomers. It provided the basis for proving that polymers of low functionality could be crosslinked to give useful soft vulcanizates. Although it follows

that the rate of a vulcanization reaction will depend on the concentration of reactive sites, it is not absolutely essential to have a multiplicity of reaction sites in order to obtain rates and states of vulcanization suitable for modern industrial practice. Thus, the useful concept of polymers with only the required low level of functionality was introduced into elastomer technology. Early in the history of studies on the vulcanization of butyl, it was shown that if the accelerator system in the vulcanization reaction is of the ultrafast type, the low functionality of the polymer would not be a major deterrent to achieving sufficiently rapid crosslinking.

Sulfur vulcanization and stoichiometry.—As in the case with other general purpose elastomers, the basic crosslinking agent for butyl polymers is sulfur.

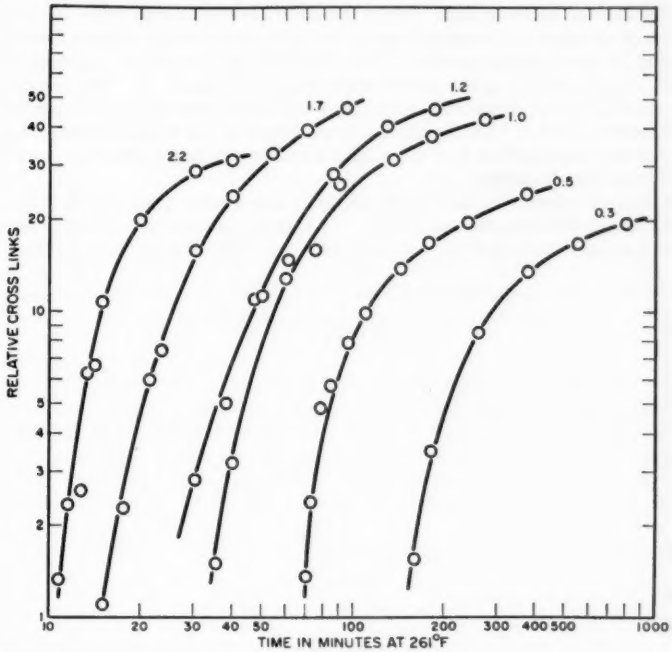


FIG. 17.—Relative crosslinks formed with respect to vulcanization time for tetramethylthiuram disulfide system. Curves are identified relative to mole per cent unsaturation of polymer used (Zapp[40]).

A major part of the development of the knowledge of the crosslinking of butyl polymers with sulfur systems is due to R. L. Zapp and his associates. The rate of crosslinking at a given vulcanization temperature for a series of fractionated butyl polymers of increasing unsaturation is given in the data of Zapp[40] in Figure 16. The state of vulcanization, indicated by equilibrium volume swell in cyclohexane at 25° C, shows a profound increase in vulcanization rate with an increase in mole per cent unsaturation from 0.3 to 2.2. It can be recognized by this that large increases in vulcanization rate into the range of practical use can be achieved without exceeding the range of unsaturation embodied in the low functionality concept.

TABLE VI

COMBINED SULFUR AT CONSTANT STATE OF VULCANIZATION DEFINED BY 1000% VOLUME INCREASE OR 18.2 RELATIVE CROSSLINKS (ZAPP[10])

Tetramethylthiuram disulfide system			Benzothiazolyl monocyclohexyl sulfenamide system		
Unsaturation	Vulcanization, minutes	Combined sulfur, %	Unsaturation	Vulcanization, minutes	Combined sulfur, %
0.3	600	0.32	0.5	230	0.47
1.0	80	0.33	0.7	120	0.40
1.2	60	0.35	1.2	81	0.40
1.7	34	0.35	1.7	61	0.41
2.2	22	0.28	1.8	59	0.42

The volume increase data yield a measure of crosslinking since the concentration of crosslinks is proportional to the 5/3 power of the volume fraction of polymer in the swollen sample. The crosslink concentration, expressed on a relative basis, is used in the plot of data shown in Figure 17. By taking data at a selected point of volume increase, or relative crosslinks, it is possible to approximate rates of vulcanization. Zapp found a linear relationship in a log-log plot of vulcanization to reach a given relative crosslink state as a function of polymer unsaturation.

It was of interest to determine whether accelerator type affected the rate and course of vulcanization of butyl. To this end the combined sulfur requirements for a selected state of vulcanization were determined for a thiuram and

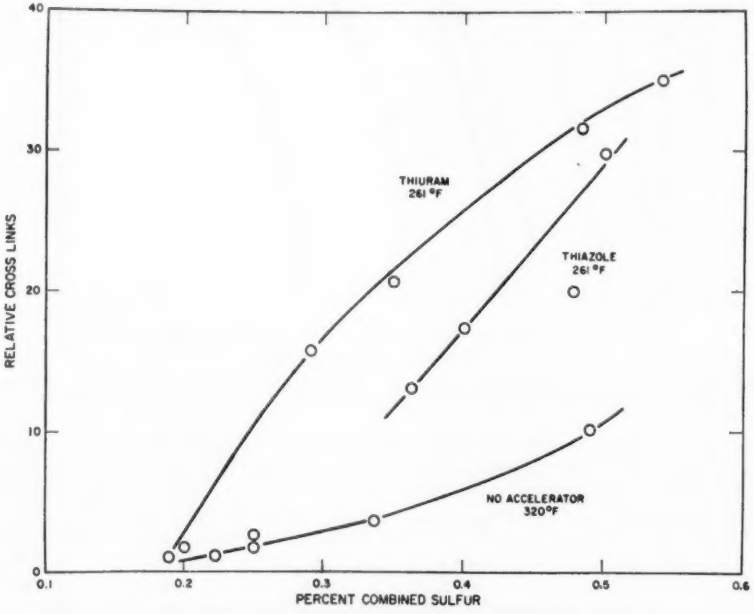


FIG. 18.—Vulcanization of accelerated and nonaccelerated butyl of mole per cent unsaturation 1.7 (Zapp[10]).

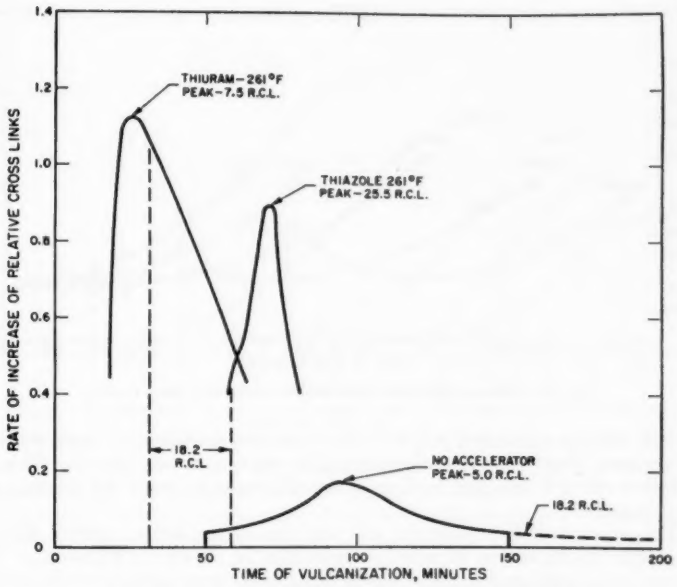


FIG. 19.—Effect of accelerator on rate and course of formation of relative crosslinks (Zapp[40]).

thiazole type accelerator. The data obtained are shown in Table VI. It is observed that the more potent thiuram requires less combined sulfur to achieve a given state of vulcanization than the thiazole type. Extending this line of research provided the provocative information shown in Figure 18. Here it may be seen that the nature of the vulcanization system has marked effect on the network achieved. For any state of vulcanization, the network achieved

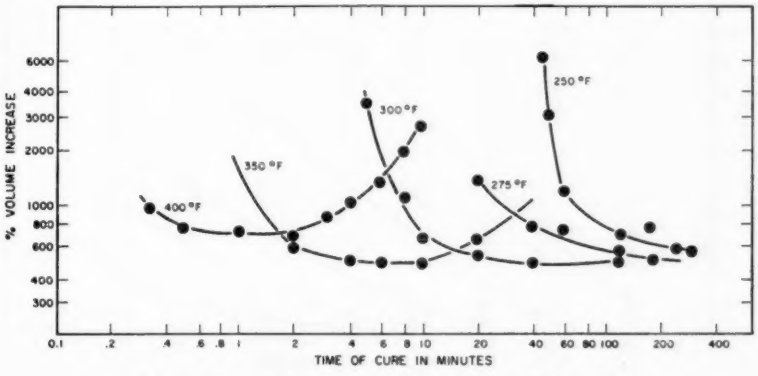


FIG. 20.—Tetramethylthiuram disulfide acceleration (Zapp et al.[41]).

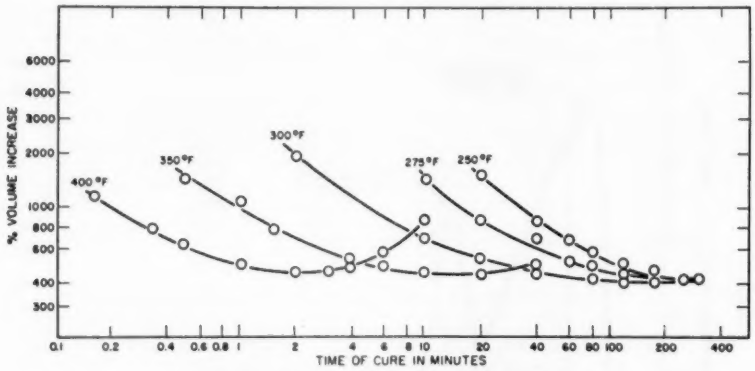


FIG. 21.—Tellurium diethyldithiocarbamate acceleration (Zapp et al.[41]).

through heating sulfur and polymer alone requires considerably more sulfur to be combined than when the polymer-sulfur reaction is accelerated. This acceleration effect is reflected further in the difference between the thiuram and thiazole types.

The presence of an accelerator and the type of accelerator control the rate and course of formation of relative crosslinks as shown in Figure 19. The differences in speed and essential characteristics of these different vulcanization systems are clearly outlined in these data.

It is important to note that Zapp measured the combined sulfur by the difference method based on the amount of sulfur extractable from the vulcanizate. This point will be referred to again later in this review. In order to reconcile the differences observed in the degree of crosslinking related to combined sulfur, this author was forced to the unsatisfactory conclusion that some of the sulfur expended in the reaction was used in an intramolecular link and thus contributed little, if any, in the restraint of the three dimensional network to the swelling

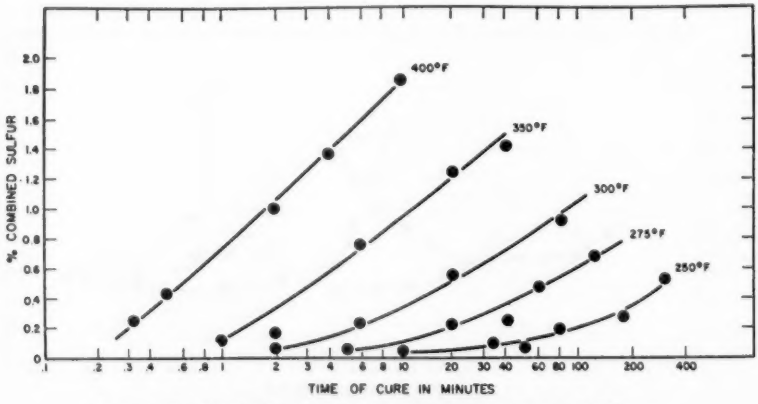


FIG. 22.—Combined sulfur versus time of vulcanization. Tetramethylthiuram disulfide acceleration (Zapp et al.[41]).

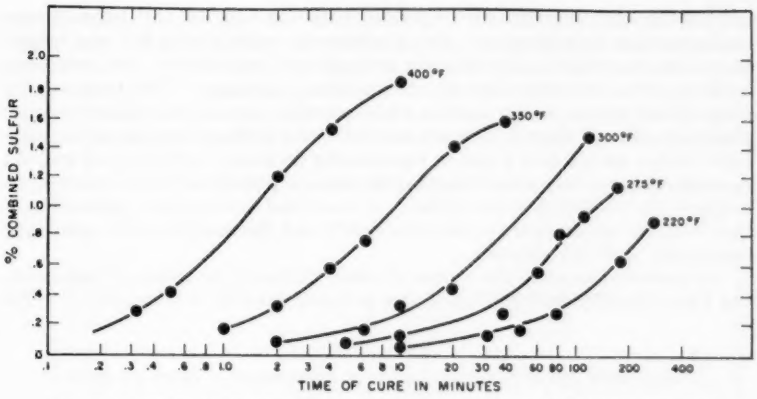


FIG. 23.—Combined sulfur versus time of vulcanization. Tellurium diethyldithiocarbamate acceleration. (ZAPP et al.[41]).

action of the solvent. From this unsatisfactory state of mind grew the work on stoichiometry of vulcanization by Zapp and associates[41].

Two types of accelerators were used in this stoichiometric work, again differing in their capacity to affect the rate of crosslinking. The accelerators used were tetramethylthiuram disulfide and tellurium diethyldithiocarbamate. Significant differences were observed when these accelerators were used in "equimolar" ratios to vulcanize pure gum butyl compositions over a range of times and temperatures. The differences may be noted by comparing the data in Figures 20 and 21. As judged by the volume swell data, the thiocarbamate-

TABLE VII

TETRAMETHYLTHIURAM DISULFIDE ACCELERATION (ZAPP ET AL.[41])

Time, minutes	Per cent volume increase	v_2 (volume fraction)	M_c (chain length)	½ (M_n/M_c) (crosslinks per average molecule)	Combined S, %	Organic S, %	Atoms combined S per average molecule	Atoms organic S per average molecule	Atoms organic S per crosslink
				At 400° F					
¼	950	0.095	26,500	3.3	0.23	—	12.57	—	—
½	750	0.118	18,000	4.86	0.44	0.16	24.02	8.74	1.8
1	720	0.122	16,900	5.18	0.74	0.38	40.41	20.74	4.0
2	730	0.120	18,000	4.86	1.03	0.59	56.3	32.33	6.6
3	870	0.103	23,200	3.77	1.26	0.77	66.8	42.05	11.2
4	1020	0.089	29,500	2.97	1.38	0.84	75.3	45.9	15.5
6	1380	0.073	51,000	1.72	1.6	1.0	87.4	54.6	31.8
10	2800	0.035	161,000	0.5	1.85	1.15	101	62.8	—
				At 300° F					
5	3600	0.027	148,000	0.6	0.16	—	8.74	—	—
8	1100	0.083	39,200	2.22	0.26	0.16	14.2	8.7	3.9
10	690	0.127	16,000	5.47	0.32	0.19	17.5	10.4	1.9
20	540	0.156	10,700	8.58	0.54	0.32	29.5	17.5	2.0
40	500	0.167	9,300	9.41	0.73	0.41	39.8	22.4	2.3
80	490	0.169	9,100	9.62	0.93	0.35	50.2	19.1	2.0
120	500	0.167	9,300	9.41	1.00	0.38	54.6	20.8	2.2
				At 250° F					
50	3000	0.032	160,000	—	0.08	—	4.4	—	—
60	1150	0.080	38,700	2.3	0.12	0.07	6.6	3.8	1.7
80	870	0.103	24,400	3.6	0.18	0.10	9.8	5.5	1.5
120	720	0.122	16,900	5.2	0.22	0.11	12.0	6.0	1.2
180	640	0.135	13,700	6.4	0.28	0.15	15.3	8.2	1.3
240	600	0.143	12,000	6.9	0.38	0.21	20.8	11.3	1.6
300	580	0.147	12,000	7.3	0.50	0.25	27.3	13.7	1.9

accelerated system produces crosslinks faster at any of the temperatures employed than does thiuram. Also, the tendency exists for the thiuram system to reverse the process of crosslinking and produce vulcanizates with increasing swelling behavior as the time of vulcanization continues. This tendency for some of the curves to turn upward with increasing time of vulcanization takes place even though there is a steady and relatively uniform increase in the combined sulfur for the two types of vulcanizates as shown in Figures 22 and 23. A distinction was then made between the total combined sulfur and the specific course of the utilization of the sulfur. It was found that a certain proportion of the combined sulfur went to form zinc sulfide and the remainder was combined organically with the polymer.

In order to ascertain the course of sulfur utilization in crosslink formation, the Flory and Rehner[42] treatment of a polymer network was employed. The

TABLE VIII

TELLURIUM DIETHYLDITHIOCARBAMATE ACCELERATION (ZAPP ET AL.[41])

Time, minutes	Per cent volume increase	v_2 (volume fraction)	M_c (chain length)	$\frac{1}{2}(M_n/M_c)$ (crosslinks per average molecule)	Combined S, %	Organic S, %	Atoms combined S per average molecule	Atoms organic S per average molecule	Atoms organic S per crosslink
				At 400° F					
¼	790	0.112	19,050	4.6	0.28	0.13	15.28	7.1	1.5
½	640	0.156	10,200	8.6	0.41	0.19	22.38	10.4	1.3
1	500	0.167	9,300	9.4	0.76	0.39	41.50	21.3	2.2
2	470	0.175	8,240	10.6	1.17	0.59	63.9	32.2	3.0
3	470	0.175	8,240	10.6	1.4	0.60	76.5	32.8	3.1
4	500	0.167	9,300	9.4	1.55	—	84.7	—	—
6	570	0.146	11,640	7.5	1.7	—	92.8	—	—
10	870	0.103	23,200	3.8	1.84	—	100.5	—	—
				At 300° F					
2	1850	0.051	91,600	1	0.06	—	8.7	—	—
4	1100	0.083	39,700	2.2	0.14	—	7.6	—	—
10	700	0.125	16,400	5.3	0.28	0.11	15.3	6.1	1.4
20	530	0.159	10,200	8.6	0.47	0.19	25.7	10.4	1.8
40	450	0.162	7,560	11.6	0.85	0.37	46.4	20.2	1.7
80	420	0.192	6,780	12.9	1.24	0.36	67.7	19.7	1.6
120	400	0.200	6,300	13.9	1.48	—	81.0	—	—
				At 250° F					
20	1460	0.064	56,400	1.6	0.09	0.05	4.9	2.7	1.7
30	1100	0.083	39,200	2.2	0.15	—	—	—	—
40	840	0.106	22,200	3.9	0.18	0.13	9.8	7.1	1.8
60	640	0.135	13,700	6.4	0.25	0.19	13.6	10.4	1.6
80	570	0.146	11,640	7.5	0.31	0.22	16.9	12.0	1.6
120	490	0.170	9,100	9.6	0.45	0.28	24.5	15.3	1.6
180	450	0.182	7,560	11.6	0.68	0.40	37.2	21.8	1.9
240	410	0.196	6,600	13.3	0.82	0.42	44.8	22.9	1.7
300	400	0.200	6,300	13.9	0.44	—	—	—	—

swelling of a network is defined in terms of the molecular weight of the chain between crosslinks, the volume fraction of polymer in the swollen gel and the molar volume of the solvent by the relationship

$$M_c = -\rho V_1 v_2^{\frac{1}{3}}/(\ln(1 - v_2) + v_2 + \mu v_2^2)$$

where M_c = molecular weight of chain between crosslinks

ρ = density of polymer

V_1 = molar volume of solvent

v_2 = volume fraction of polymer in swollen gel

μ = solvent polymer interaction coefficient

It was necessary to obtain a value for μ in the solvent cyclohexane. Huggins[43] had obtained a value of 0.41 for polyisobutylene using osmotic pressure methods. Flory[44], by relating tension at a given degree of elongation to equilibrium swelling in cyclohexane at 25° C, found a value of 0.3 for a butyl vulcanizate. Using the technique of Doty and Zable[45] on lightly crosslinked networks, Zapp established a value of 0.35 for butyl vulcanizates. It was now possible

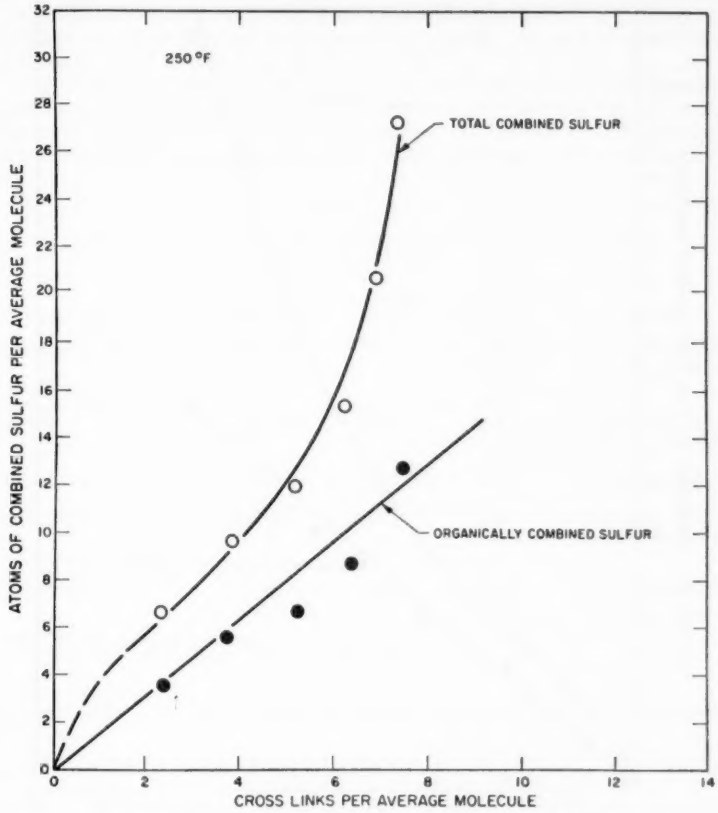


FIG. 24.—Relation of combined sulfur to cross links. Tetramethylthiuram disulfide acceleration (Zapp et al.[41]).

to provide a stoichiometric basis of the sulfur vulcanization of butyl. These data relating sulfur utilization to the crosslinked network are shown in Table VII for the thiuram system and in Table VIII for the thiocarbamate system. These stoichiometric records afford a very useful set of data for further inquiry into the nature of vulcanization.

This work began to lay the basis for a possible solution to the "anomolous" relation between combined sulfur and the state of the crosslinked network. A

clearer understanding of the competitive constructive and destructive reactions possible during the vulcanization process was beginning to evolve. The tendency of the volume increase curves to all show minima with time of vulcanization suggested that the crosslinked density was a sum of at least two reactions. The marked tendency for the vulcanizates to revert suggested that if sulfur were being consumed with increased time of vulcanization, it could not possibly

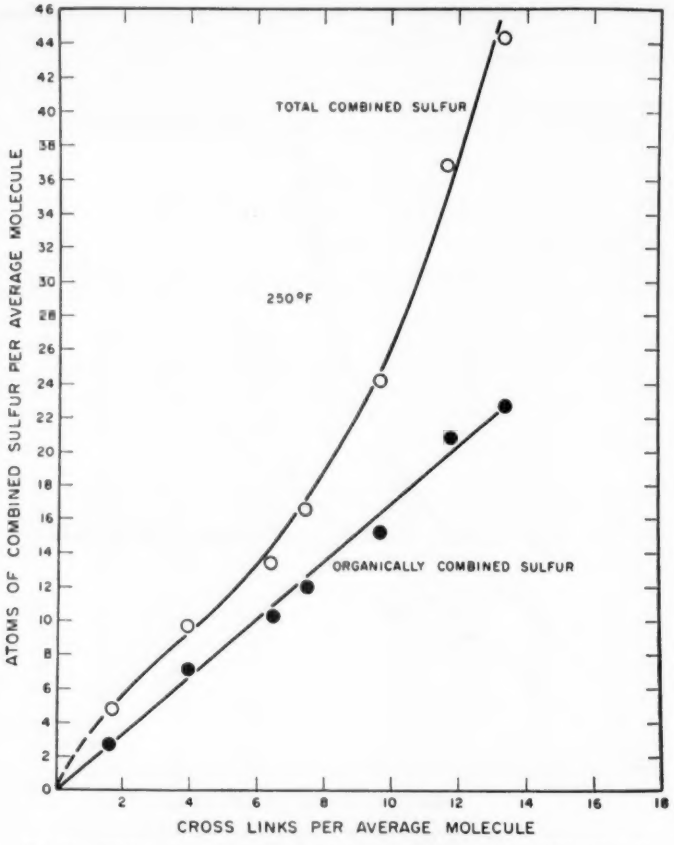


FIG. 25.—Relation of combined sulfur to cross links. Tellurium diethyldithiocarbamate acceleration (Zapp et al[41]).

be forming the crosslinks of a stable network. This is shown dramatically in the case for the tetramethylthiuram disulfide system vulcanized at 400° F. This work indicated that a butyl vulcanizate (at an optimum point in the volume swell-vulcanization time curve) contained about two atoms of sulfur per crosslink. The well-known instability of disulfide and polysulfide linkages began to assume a definite place in the analysis of this work. It was postulated

that when combined sulfur did not contribute to the crosslink network, it was due to severing of the disulfide bond formed during vulcanization leaving the combined sulfur in an uncrosslinked form. This postulate is supported by the indications of the plots in Figures 24 and 25. It should be noted that the essential feature of these representations of the data is the *relationship of atoms of combined sulfur per average molecule* as a function of *crosslinks per average molecule*. This shows clearly that large amounts of sulfur can be consumed under certain conditions in the vulcanization process without contributing to the crosslink network. Since it is not in the form of zinc sulfide, it must be organically combined with the polymer *but not in a crosslink*.

It is of interest that this work provides an explanation for the oft-repeated observation that the tension properties of vulcanizates bear little relation to the amount of sulfur utilized in their preparation. It follows that if combined sulfur is defined in terms of the amount of sulfur effecting stable crosslinks, then

TABLE IX

REVERSION AND MERCAPTAN CONTENT IN BUTYL VULCANIZATES (ZAPP AND FORD[46])

Vulcanization	Accelerator*	Volume swell, %	% S as mercaptans	Remarks
80 minutes at 300° F	TMTDS	360	0.23	Overnight shaking
			0.17	ultrasonic vibrator
80 minutes at 300° F plus 30 minutes at 400° F	TMTDS	1560	0.70	Overnight shaking
			0.83	ultrasonic vibrator
Degraded in H_2S atm	TMTDS	Soluble	1.02	Overnight shaking
80 minutes at 300° F	TDEDC	310	0.07	Overnight shaking
			0.03	ultrasonic vibrator
80 minutes at 300° F plus 30 minutes at 400° F	TDEDC	480	0.11	Overnight shaking
			0.30	ultrasonic vibrator

* TMTDS = tetramethylthiuram disulfide acceleration.
TDEDC = tellurium diethyldithiocarbamate acceleration.

there should be a definite relationship between sulfur so utilized and the tension properties.

Sulfur vulcanization and reversion.—Zapp and Ford [46] showed that the course of the extended time of vulcanization or reversion was the formation of mercaptans. This is shown in Table IX. It is of interest that the original three dimensional network can be degraded to a soluble form by heating in an atmosphere of H_2S with the formation of a large concentration of mercaptan sulfur in the vulcanizate. The vulcanizates subjected to further heating mirror this same tendency. In view of the essential role assigned by Craig and associates[47] to H_2S in the various reactions possible in the vulcanization process, it would appear that this material could account for the phenomenon of reversion under the proper conditions. Zapp and Ford postulated that the H_2S promoted the cleavage of the S—S link with the formation of thiols.

In further studies on reversion, these authors showed that the tendency towards reversion could be markedly reduced by the presence of metallic per-

oxides. An example from their work is shown for calcium peroxide in TableX. The presence of 8 phr of calcium peroxide reduces the concentration of mercaptan sulfur formed by a a factor of almost 3 and with consequent higher retention of the crosslink density of the network. Although the use of these peroxides has a practical limitation (molecular weight breakdown on heating), it would appear that their action in inhibiting the reversion process is a useful key to further study of this aspect of vulcanization and network stability.

A major contribution to the end use of butyl resulted from these advancements of the knowledge of the sulfur-crosslinking process. Early development of butyl vulcanizates for application where flexing was of importance encountered severe reversion. The exact nature of this result was not clearly understood. In the main, however, it was attributed to the hysteretic properties of the polymer. The progress of research on sulfur vulcanization, discussed in this review, pointed to a possible amelioration of the situation if some of the ill effects of the chemistry of reversion could be shown to be a co-cause of sample or product degradation on flexing. It was observed that if careful attention were paid to the amount of sulfur actually needed for a given crosslink density,

TABLE X

RETARDATION OF THIOL GROUP FORMATION WITH CALCIUM PEROXIDE (ZAPP AND FORD[46])

Vulcanization	Composition*	Volume swell, %	Mercaptans, %	Remarks
10 minutes at 350° F	TMTDS control	520	0.16	Overnight shaking
			0.12	Overnight shaking
			0.11	ultrasonic vibration
80 minutes at 350° F	TMTDS control	1440	0.54	Overnight shaking
10 mintes at 350° F	TMTDS + CaO_2	490	0.06	Overnight shaking
			0.10	ultrasonic vibrator
80 minutes at 350° F	TMTDS + CaO_2	740	0.20	Overnight shaking

* TMTDS = tetramethylthiuram disulfide acceleration.

together with the organic accelerator employed, a major improvement in flexing behavior resulted.

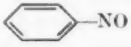
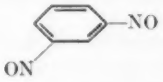
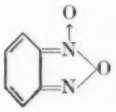
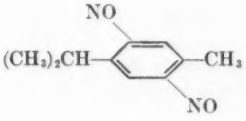
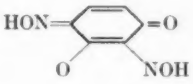
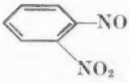
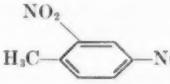
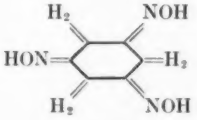
It may be noted further that there is a growing realization among those doing research on polymers that there is probably a very close connection between the process of vulcanization and the mechanism of degradation. One of the first points of recognition of this probability is embodied in the vulcanization research just discussed.

Crosslinking with polynitroso compounds.—The crosslinking of butyl with polynitroso compounds represents the major field of vulcanization of this polymer in the past without the use of sulfur. Rehner and Flory[48] studied the action of dinitroso, dioxime and related compounds in butyl. The vulcanizing activity of a number of dinitroso and related compounds, as given in their work, is shown in Table XI. A number of the compounds shown which are inactive were classified as not being true dinitroso compounds.

These authors selected 2-methyl-2-butene and 1-pentene as analogs of the double bond reactivity in 1,4 isoprene addition to the chain and 1,2 and 3,4 addition, respectively. These olefins were heated with quinone dioxime in the

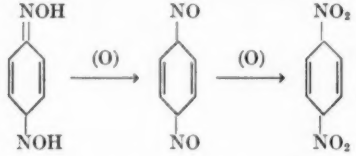
TABLE XI

VULCANIZING ACTIVITY OF DINITROSO AND RELATED COMPOUNDS IN BUTYL (FLORY AND REHNER[48])

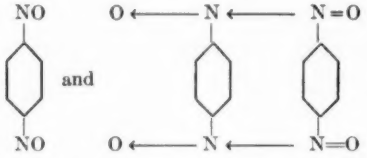
Compound	Probable monomolecular formula	Vulcanizing activity
Nitrosobenzene		Inactive
p-Dinitrosobenzene		Very active
m-Dinitrosobenzene		Very active
o-Dinitrosobenzene		Inactive
Dinitrosocymene		Very active
2,4-Dinitrosocresorcinol		Inactive
o-Nitronitrosobenzene		Inactive
o-, *m*-, or *p*-Dinitrobenzene		Inactive
2,4-Dinitrotoluene		Inactive
Phloroglucinol trioxime		Inactive

presence and absence of Pb_3O_4. No significant amount of reaction product was formed with the 1-pentene analog upon extended heating, whether the red lead oxide was present or not. The amount of reaction product with the 2-methyl-2-butene analog increased with time and was increased further several fold by the presence of the red lead oxide. These authors concluded that the 1,4 isoprene structure of butyl with its double bond situated in the chain would be reactive towards quinone dioxime and the reaction would be increased by the presence of the red lead oxide. However, when an attempt was made to translate these results to butyl, it became obvious that the quinone dioxime was not capable of affecting the crosslinking without the presence of an oxidizing agent. In the course of this work, these authors also showed that chemical unsaturation in the polymer chain was necessary since polyisobutylene could not be crosslinked by these agents.

The seemingly important role of the oxidizing agent suggested that perhaps the effective vulcanizing agent is an oxidation product of the dioxime. The continued oxidation of this compound should give these products.



These authors considered that in hydrocarbon solution *p*-dinitrosobenzene consists of an equilibrium mixture of the following structures.

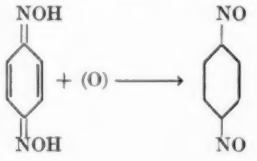


In this mixture, the equilibrium favors the bimolecular form.

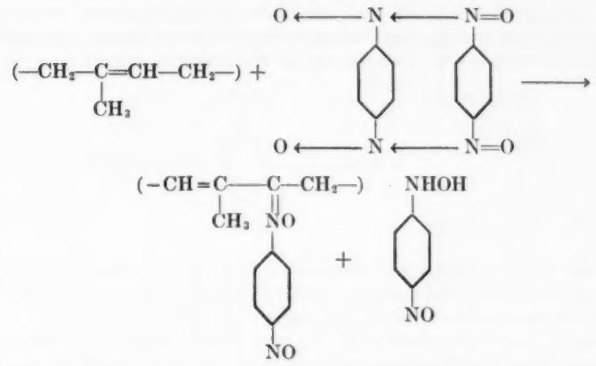
It was found that *p*-dinitrosobenzene is an extremely active vulcanizing agent for butyl even at very low concentrations. Furthermore, the presence of an oxidizing agent was not necessary. The *p*-dinitrobenzene was found to be completely inactive and this inactivity was unchanged by the presence of oxidizing agents.

The theory of vulcanization evolved in this work may be treated as follows in the successive steps.

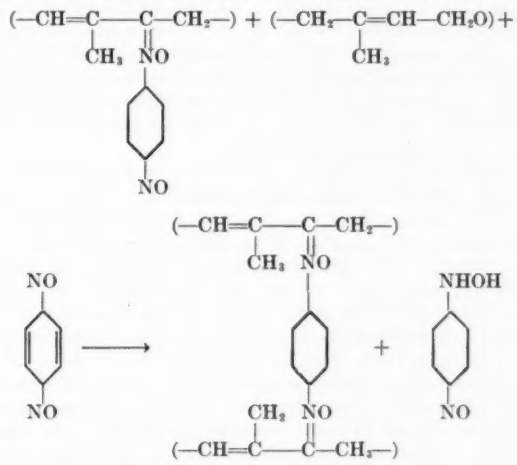
Oxidation of dioxime to nitroso



Reaction of nitroso with diolefin unit of the polymer chain and formation of p-nitrosophenyl hydroxylamine



Crosslinking through free nitroso group and diolefin unit of another chain

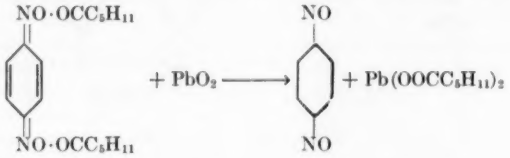


These authors suggest that the *p*-nitrosophenyl hydroxylamine rapidly rearranges to form quinone dioxime.

Confirmation of the proposed mechanism of vulcanization was based on examination of a sample of butyl reacted with *p*-dinitrosobenzene and then exhaustively extracted with three solvents. It was argued that this examination should show the presence of chemical unsaturation, combined nitrogen and extractable quinone dioxime. Experimental difficulties with the unsaturation procedures allowed only the qualitative conclusion that unsaturation was present. The actual data showed an increase from 0.6% for the original butyl to 2.7% for the extracted vulcanizate. Assuming that the crosslinking step proceeded as shown, the calculated nitrogen content should be 0.18%. The nitrogen content found by analysis was 0.25%. A crystalline product from the

extract showed very close agreement with the carbon, hydrogen and nitrogen content of quinone dioxime.

Flory and Rehner suggest that the esters of the dioximes, which are also effective vulcanization agents, first go to the dinitroso form. An example of this reaction is shown with lead dioxide as the oxidizing agent.



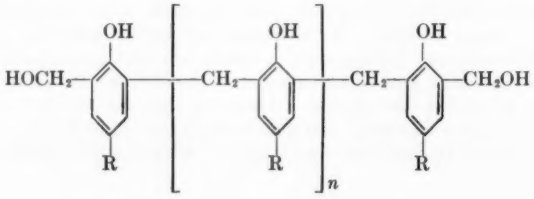
As a test of the validity of the suggested step, these authors reacted quinone dioxime caproate with lead dioxide. Lead dicaproate was found in the reaction mixture in an amount in approximate agreement with the equation.

Although it has been shown that polymer unsaturation is necessary for the crosslinking of butyl with *p*-dinitrosobenzene, it has subsequently been observed that the rate or state of reaction of butyl with this agent is not very sensitive to the unsaturation level of the polymer. Whereas in the sulfur crosslink system a direct relation is established for reaction rate dependence on unsaturation, no such dependence is observed with *p*-dinitrosobenzene. Other aspects of this field of vulcanization which would arouse scientific curiosity are the great speed of the reaction particularly at low temperatures, the mechanical properties of the vulcanizates derived from the use of dinitroso crosslinking agents and the marked resistance to oxidative degradation.

It would appear to be of value in view of the preceding remarks on this type of vulcanization system to study its stoichiometry. Thus, an attempt could be made, as Zapp did for sulfur vulcanization, to relate molecules of dinitrosobenzene consumed to the number of crosslinks formed during vulcanization. This type of research could provide information on how much of the dinitrosobenzene reacted (1) with itself, (2) with one chain diolefin unit but not forming a crosslink and (3) with diolefin units in two chains forming a crosslink.

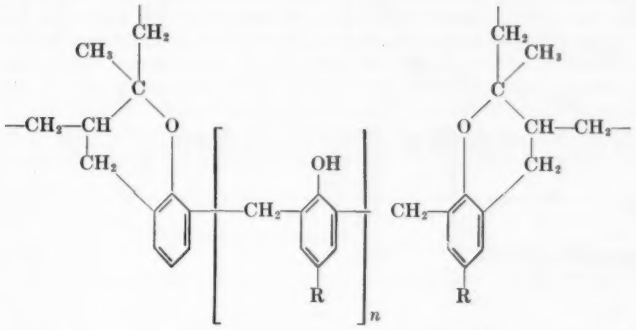
Crosslinking with methylolphenol resins.—Two new fields of crosslinking of butyl have recently opened. One of these fields is the vulcanization of butyl with polymers derived from the condensation of 2,6-dimethylol-4-hydrocarbyl phenols. The other field is the advent of halogen containing isobutylene-isoprene copolymers such as MD-551 (chlorine), MD-572 (bromine) and Hycar 2202 (bromine). These two events thus represent the availability of two new (essentially nonsulfur) crosslinking systems for the copolymer of isobutylene and a diolefin.

Tawney, Little and Viohl[49] discussed the vulcanization of butyl rubber with phenol formaldehyde derivatives of the type 2,6-dimethylol-4-hydrocarbyl phenols. A simplified representation of the polymer is given by these authors as follows.

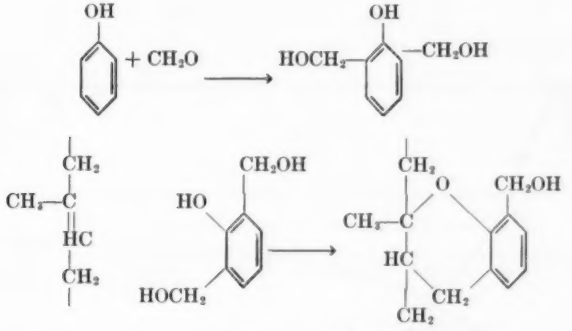


where R is an alkyl or hydrocarbyl group and n may vary from 0 to 5 or 6. The methylene groups are also indicated as being replaceable by $CH_2—O—CH_2$ groups.

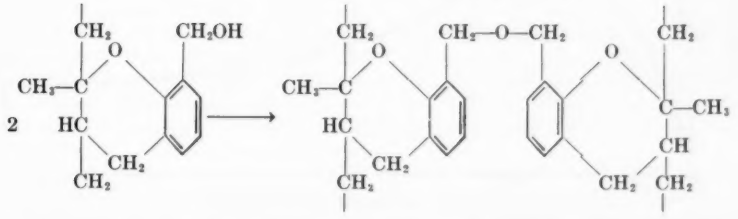
The suggested crosslink structure for this material with butyl is given by the authors as follows.



This is the chroman structure postulated by Greth[50] for reaction of phenolic formaldehyde compounds with the double bond of the isoprene unit in natural rubber. For simplicity's sake, a monomeric form of the resin is used in the illustration.

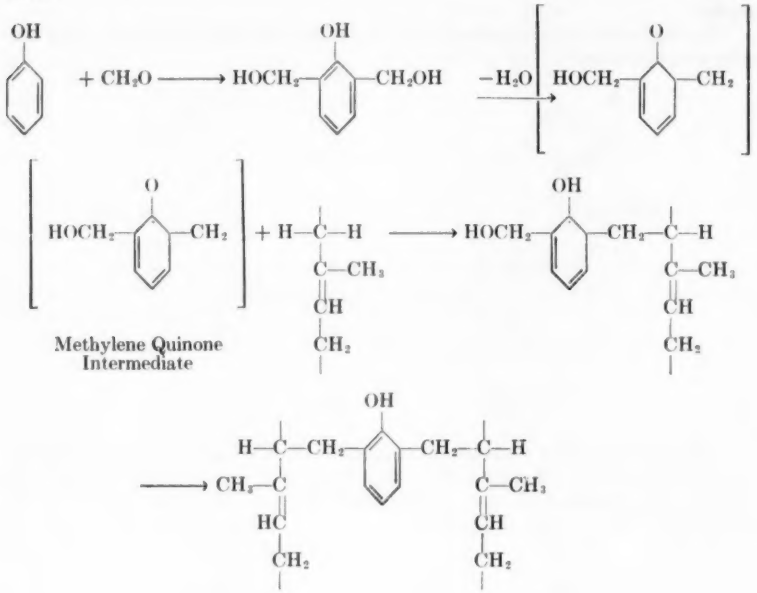


Chroman Structure



An alternate structure, not involving the double bond, suggests a reaction through a methylene quinone derivative with the isoprene unit of natural

rubber. This structure derived from the work of Van der Mer[51] could apply here.



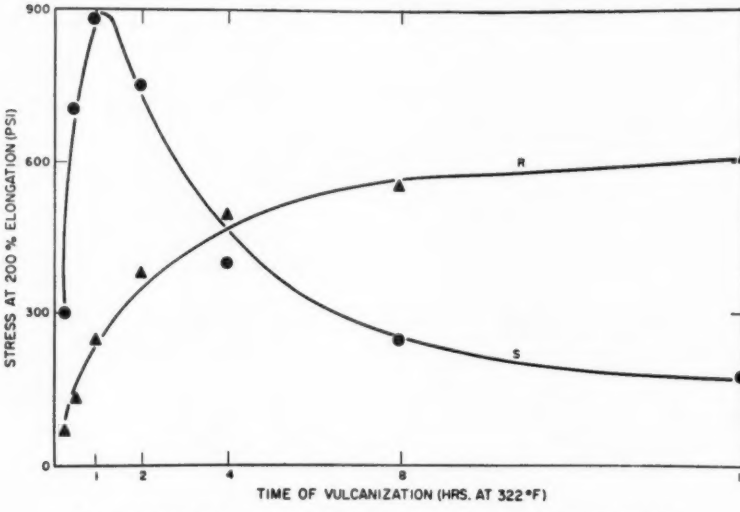


FIG. 26.—Vulcanization of butyl with a sulfur-accelerator system (S) and a phenolic condensation resin (R) (Tawney, Little, and Viohl[49]).

A comparison of vulcanization as a function of time for a sulfur system and methylol resin is shown in Figure 26 taken from the publication of Tawney, Little and Viohl. The vulcanization comparison shows two distinct differences as judged by the stress measurement: (1) the methylol system is considerably slower, and (2) the methylol system has a much greater stability towards increased exposure to vulcanization conditions than is the case with the sulfur system. Although the vulcanization times are extensive, they are useful in predicting the stability of the vulcanizates to prolonged heat exposure.

Considerable improvement in the rate and state of vulcanization can be obtained by catalyzing the action of the methylol resin with metallic halides such as $FeCl_3 \cdot 6H_2O$, $ZnCl_2$ and $SnCl_2 \cdot 2H_2O$. The effect is concentration dependent as shown in Figure 27 for the system employing $SnCl_2 \cdot 2H_2O$. These authors also show that for a given concentration of the resin, a normal response

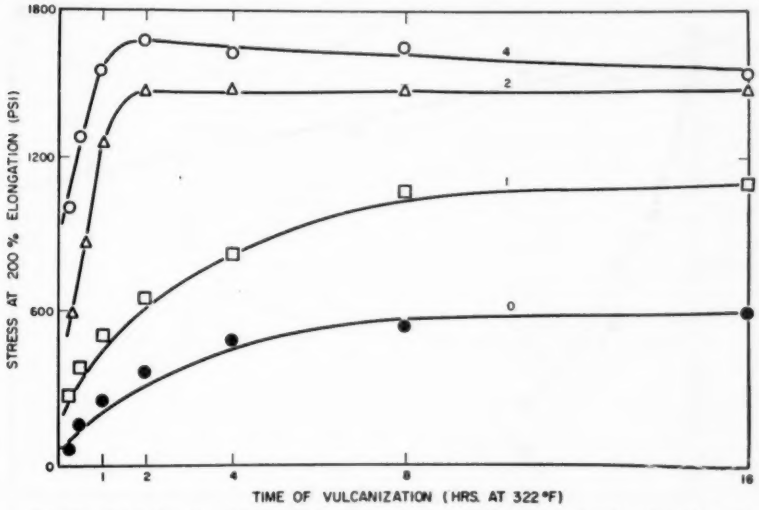


FIG. 27.—Catalytic action of $SnCl_2 \cdot 2H_2O$ in the vulcanization of butyl with phenol condensation resin. All vulcanizates contain 6 phr. of resin. Curves are identified as to stannous chloride dihydrate concentration in phr (Tawney, Little, and Viohl[49]).

(increase in rate of vulcanization) is obtained with increasing unsaturation of the butyl polymer. All the curves begin to approach an asymptote with respect to concentration at about 12 phr.

The new vulcanizing system endows the butyl polymer with an increased level of resistance to degradation when aged in air. The decay in tensile strength is compared to that of a vulcanizate from a sulfur system in Figure 28. A dramatic difference in resistance to aging is evident. The difference would appear to be equivalent to about 100° F higher allowable temperature of exposure for a given tensile strength decay.

It is of interest to note that Van der Meer found that if the methylol grouping in the phenolic compound was para to the hydroxyl grouping, crosslinking proceeded as well as with the ortho structure. It is difficult therefore to visualize the crosslinking process occurring by the chroman route in such a case. The

position of the methylol grouping would have lesser effect in controlling vulcanization by the methylene quinone intermediate route. These general reactions are discussed by Miller and Robison[52] in a paper related to phenolic formaldehyde compounds in tire cord adhesive compositions.

Halogen containing copolymers.—The advent of halogen containing copolymers of isobutylene and isoprene was a major step in the development of crosslinking systems for this type of polymer. The major part of the discussion herein will be related to the Enjay Company market development product MD-551, which contains chlorine[53]. The chlorine content of MD-551 is about 1.1 to 1.3 per cent. The unsaturation is about one mole per cent. Specific gravity is 0.92. The Mooney viscosity is 52 ± 5 for an eight minute test at 212° F. The viscosity average molecular weight is about 400,000. The raw polymer is completely soluble in hydrocarbon solvents and contains no gel.

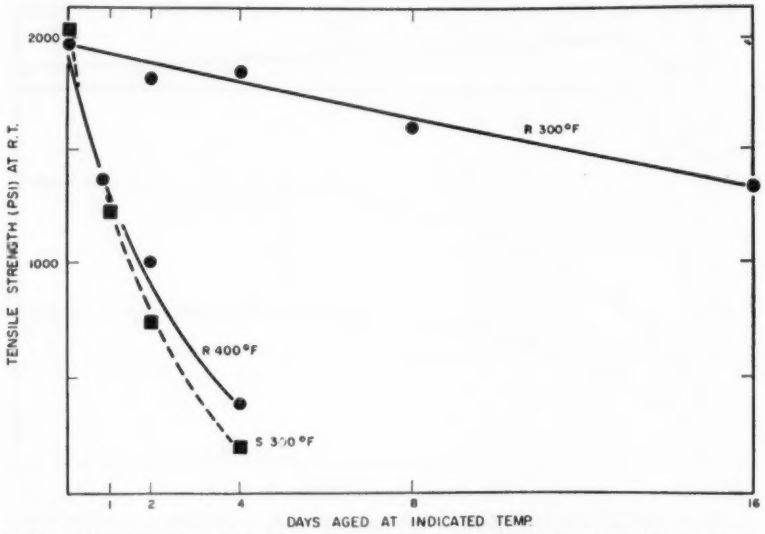


FIG. 28.—Comparative aging of butyl vulcanized with sulfur-accelerator system (S) and phenol condensation resin (R) (Tawney, Little, and Viohl[49]).

The importance of this type of polymer to the butyl development is in the change of functionality. Whereas the conventional isobutylene-isoprene copolymers rely on the functionality of allylic hydrogen for the crosslinking process, MD-551 contains the functionality of chlorine. This polymer can be vulcanized with the normal systems such as sulfur-accelerators, quinones, methylol resins, as well as new crosslinking systems not heretofore applicable to isobutylene-isoprene copolymers.

One of the unique features of this polymer is the ability to crosslink through the agency of zinc oxide alone. A typical set of tension data for a simple HAF composition crosslinked with zinc oxide alone is shown in Figure 29. It is conceivable that some of the crosslinks formed in this vulcanization are carbon-carbon bonds. It is known that zinc chloride is formed as a product of this vulcanization system.

A very appreciable increase in the rate of vulcanization of MD-551 occurs if tetramethylthiuram disulfide is used along with zinc oxide. An example of this is shown in Figure 30. In this particular case, the crosslink may be carbon to carbon and/or C—S—C bonds.

MD-551 may be expected to vulcanize in the normal way with sulfur-accelerator. The chlorine atom appears very reactive in a formulation which would be used for sulfur vulcanization. The vulcanization of this polymer with zinc oxide-sulfur-thiocarbamate is shown in Figure 31 in comparison with that of Enjay Butyls 218 and 325.

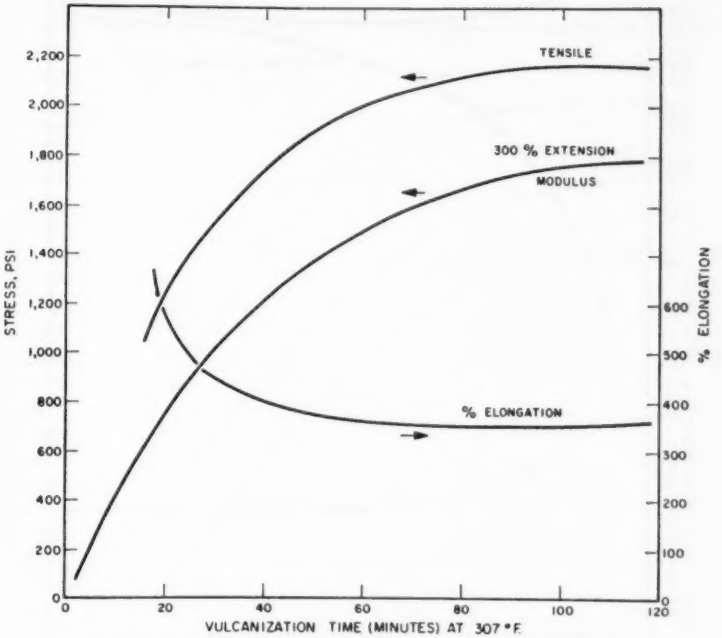


FIG. 29.—Vulcanization of MD-551 with zinc oxide as sole crosslinking agent—5 phr (Eby and Fusco[58]).

Quinone dioxime (GMF) is an effective crosslinking agent for butyl and is also effective in MD-551. In order to compare these polymers under the best conditions, the following formulations were used for the two types of vulcanizates.

	Enjay Butyl 218	MD-551
Polymer	100	100
HAF carbon black	50	50
Stearic acid	0.5	1.0
Zinc oxide	5.0	5.0
Benzothiazolyl disulfide	4.0	4.0
Red lead (Pb_3O_4)	5.0	—
Lead dioxide (PbO_2)	—	2.0
Quinone dioxime	1.5	2.0

Data for these crosslinking systems are shown in Figure 32. It may be noted that the rate of vulcanization for MD-551 is somewhat slower with this crosslinking system than is the case with Enjay Butyl 218.

The active chlorine present in MD-551 offers new avenues for crosslinking the copolymer. One of these, metallic oxides, has already been discussed with zinc oxide as an example. Another new crosslinking agent is represented by the polyamines. It is of interest that monofunctional amines will also crosslink

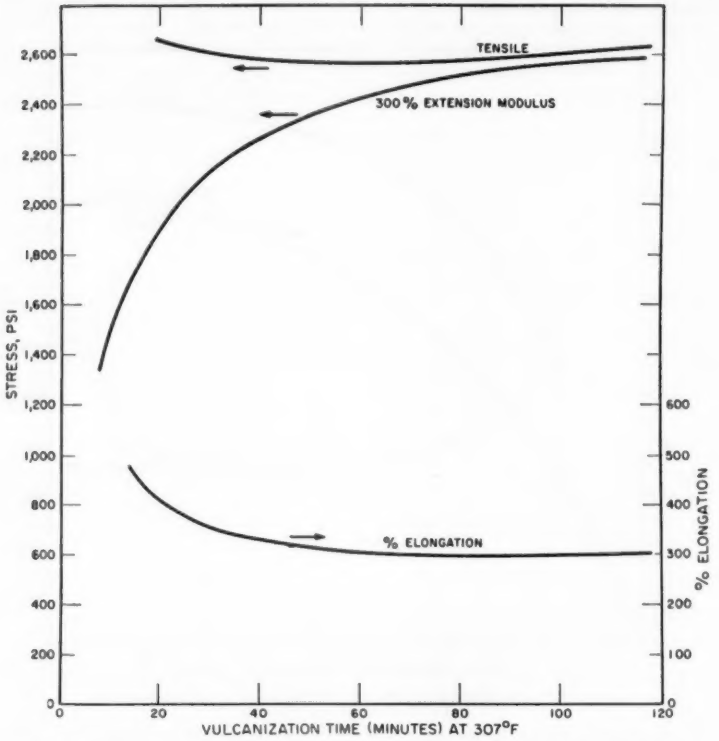


FIG. 30.—Vulcanization of MD-551 with combined zinc oxide, 5 phr, and tetramethylthiuram disulfide, 1.0 phr (Eby and Fusco[53]).

this polymer although the reaction is much slower. It has been observed that magnesium oxide may be an important part of this reaction.

MD-551 may be crosslinked with the methylolphenol resin system. There are essential differences in the efficiency of this vulcanizing reaction in MD-551 as compared to its action in commercial Enjay Butyl polymers. The rate of vulcanization is considerably faster and the vulcanization process does not require the presence of another halogen containing compound, such as zinc chloride, normally required with the Enjay butyl polymers and this material.

Morrissey[54] discussed butyl-type polymers containing bromine. The com-

mercial product related to this work is now known as Hycar 2202 (B. F. Goodrich Chemical Company). A comparison of vulcanization rate for butyl and brominated butyl from the work of Morrissey is shown in Figure 33. The composition used here contained 50 phr of EPC black and contained zinc oxide—5.0, benzothiazolyl disulfide—0.5, tetramethylthiuram disulfide—1.0 and sulfur—2.0 parts per hundred as the vulcanizing system. It may be seen that the increase in the rate of vulcanization due to the presence of bromine is of the same order as that noted for the chlorine containing copolymer, MD-551.

One of the interesting aspects of the halogen containing polymers is improvement in compatibility with high diene polymers such as natural rubber

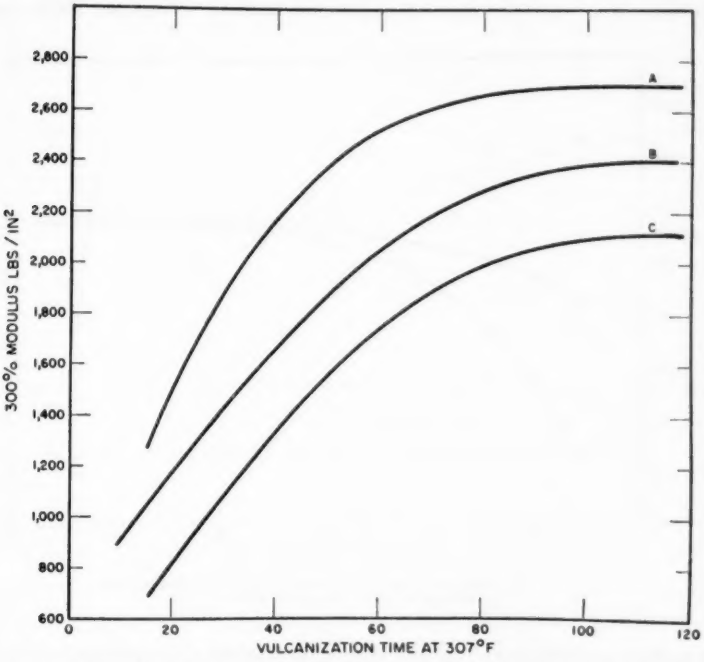


FIG. 31.—Comparative vulcanization of MD-551 (A), Enjay Butyl 325 (B), and Enjay Butyl 218 (C). The vulcanization system used with all three polymers was sulfur—2.0, zinc oxide—5.0, and tellurium diethyldithiocarbamate—1.0 phr (Eby and Fusco[48]).

and SBR. This "compatibility" is capable of evaluation in a certain sense by tensile strength measurements. It is believed that the change in compatibility over that of the isobutylene-diolefin copolymer is somehow related to a change in the vulcanization mechanism. Tensile strength data for various ratios of natural rubber and brominated butyl are shown in Figure 34. The composition used here contained 30 phr HAF and was vulcanized with zinc oxide—5.0, benzothiazolyl disulfide—1.0, diorthotolylguanidine—0.1 and sulfur—2.0. It can be noted that when the isobutylene-diolefin copolymer is used, the mechanical properties of the resultant vulcanizates as evidenced by the tensile

strength level are very low, indicating a very heterogeneous system. Morrissey showed that blends of brominated butyl and SBR also gave high tensile strengths. In view of this demonstrated compatibility of the vulcanizing system, it was envisioned that bonding between natural rubber and this polymer should be improved. Adhesion data for the bonding of brominated butyl to a 50–50 mixture of SBR-natural rubber are shown in Figure 35. The variable under study in this work is the polymer content of the adhesive tiegum. It is shown that adhesion is increased from 20 to 72 pounds pull per inch of width in this test as the ratio of brominated butyl to natural rubber progresses from 100/0 to 60/40.

It is of interest to know how the properties of the polymer relative to vulcanization may vary as a function of bromine content. Morrissey shows data

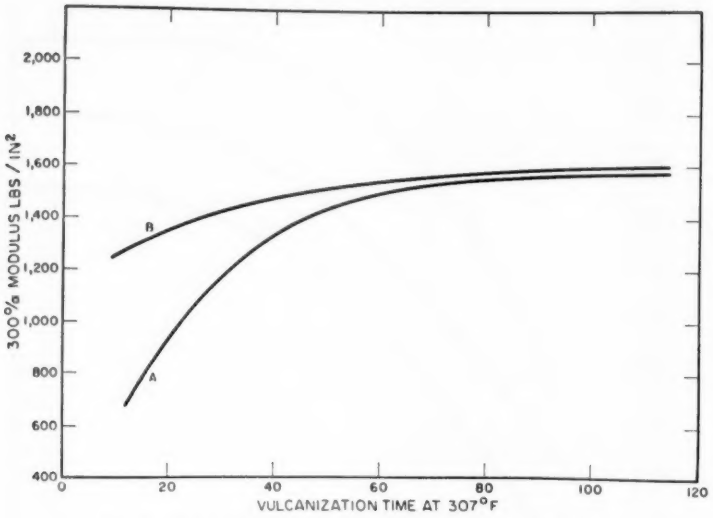


FIG. 32.—Vulcanization of MD-551 (A) and Enjay Butyl 218 (B) with quinone dioxime (Eby and Fusco[48]).

for tension properties as a function of bromine content of the polymer in Figure 36. Tension properties such as modulus at 300 per cent extension are related to the crosslink density achieved under given conditions of vulcanization. It may be noted that in the range of 2–3 per cent bromine in the polymer, this property increases in approximately linear fashion. The ultimate extensibility reflects a similar relationship while tensile strength is only mildly affected. The tension data shown are what would be expected from a vulcanization system made more active by addition of bromine to the polymer.

Morrissey[55] extended his work to a consideration of the halogenation of butyl rubber with iodine monochloride and iodine monobromide. This work is essentially an attempt to improve on the knowledge of the halogenation of butyl with bromine.

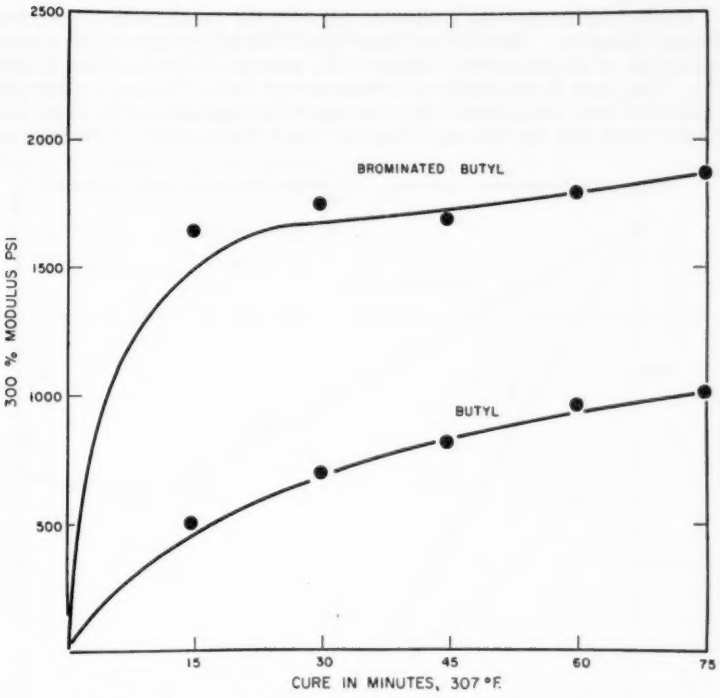


FIG. 33.—Comparison of modulus of butyl and brominated butyl (Morrissey[44]).

TABLE XII

EXTRAPOLATED VALUES OF THERMAL DIFFUSIVITY FOR VARIOUS POLYMERS (REHNER[6])

Polymer	Compound type	$k \times 10^4$ cm²/sec 60° C	$k \times 10^4$ cm²/sec 140° C	$\frac{\Delta k}{\Delta T° C} \times 10^4$
Butyl	Pure gum	0.89	0.51	0.48
Hevea	Pure gum	1.06	0.59	0.59
SBR	Pure gum	1.24	0.57	0.84
Butyl	Polymer 100 Plasticizer[a] 20	0.93	0.46	0.59
Hevea	Polymer 100 Plasticizer[a] 20	1.05	0.60	0.56
Butyl	Polymer 100 EPC black 54 Plasticizer[a] 20	1.34	0.65	0.86
Hevea	Polymer 100 EPC black 54 Plasticizer[a] 20	1.49	0.92	0.71

[a] Hydrocarbon oil.

Thermal diffusivity.—An important aspect of the crosslinking of butyl is its thermal diffusivity. MacRae and Zapp[56] presented information on this polymer and certain of its compounds, together with examples of applicability to practice. This work is essentially a continuation of that of Rehner[12] whose data relative to butyl and certain other elastomers are summarized in Table XII. Rehner found that the thermal diffusivity was a characteristic of the polymer.

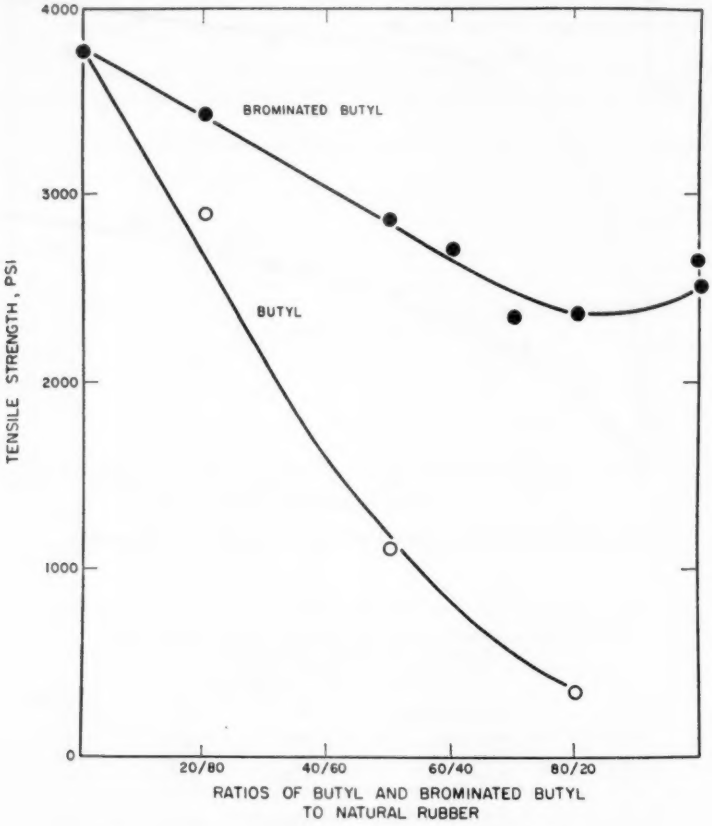


FIG. 34.—Effect of brominated butyl on tensile properties of blends with natural rubber (Morrissey[54]).

Of the compounding ingredients which might be used in high volume, carbon black was found to have a large effect and oil plasticizer very little effect. Further, it was observed that the thermal diffusivity of the polymers decreased almost linearly with the temperature. From this work, it would appear that both diffusivity and the related thermal conductivity for compositions can be calculated to a good degree of approximation as follows.

$$\text{Thermal diffusivity} = \sum_{i}^{n} \sqrt{n}\, k_n$$

$$\text{Thermal conductivity} = \sum_{i}^{n} \sqrt{n}\, k_n\, c_n\, d_n$$

where $\sqrt{n}$ = volume fraction of material n
k_n = thermal diffusivity of material n
c_n = heat capacity of material n
d_n = density of material n

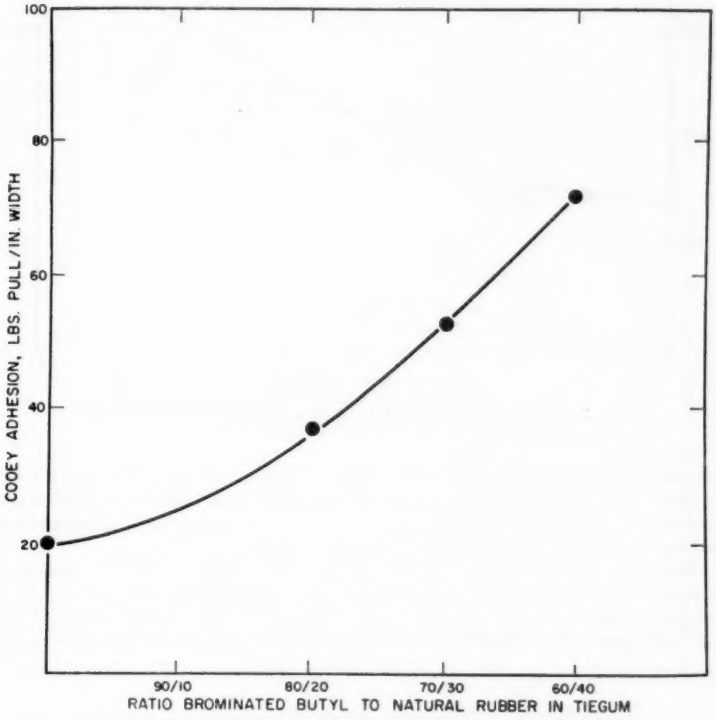


FIG. 35.—Effect of tiegum variation on 212° F adhesion to 50:50 SBR and natural rubber (Morrissey[84]).

The data of MacRae and Zapp for the variation of thermal diffusivity with temperature for a number of carbon blacks is shown in Figure 37. Determination of the effect of black on thermal diffusivity showed an inconsistent relation with particle size although large differences in the effect over a pure gum vulcanizate were noted. This would appear to be an interesting field of research

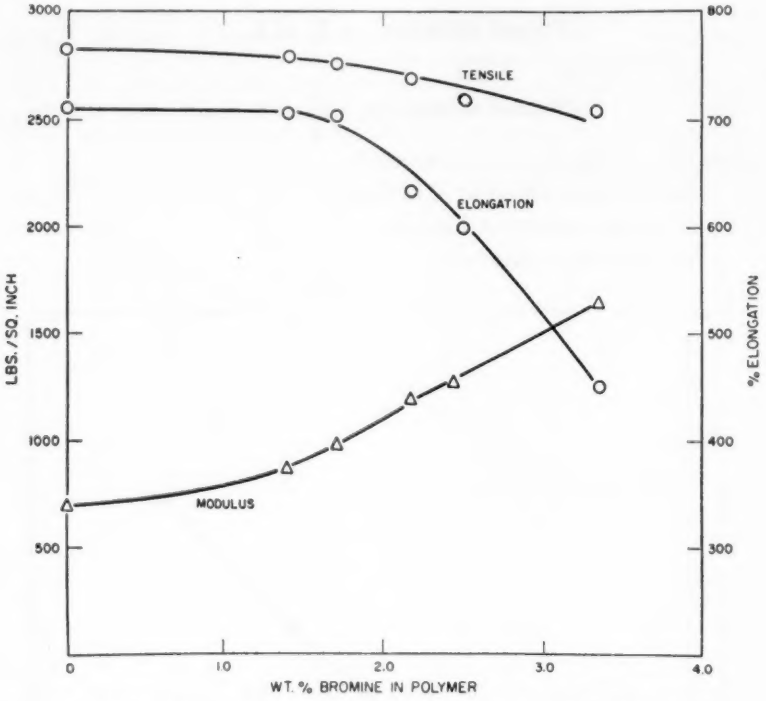


FIG. 36.—Effect of increasing amounts of bromine on stress-strain properties of brominated butyl (Morrissey[54]).

and may have some relation to the state of agglomeration of the black in the polymer. Butyl is found to have a lower thermal diffusivity than other elastomers such as SBR and natural rubber and this is an important consideration in comparing rates of vulcanization on a strict basis.

Temperatue coefficient of vulcanization.—The temperature coefficient of vulcanization is important in relation to the temperature dependence of the reaction rates involved in the process of vulcanization. Lowenstein and Rollins[57] tabulated the temperature coefficients for a number of elastomers includ-

TABLE XIII

TEMPERATURE COEFFICIENTS OF VULCANIZATION FOR VARIOUS ELASTOMERS (LOWENSTEIN AND ROLLINS[57])

Polymer	Temperature coefficient for 10° F
Natural rubber	1.6
Nitrile (Perbunan)	1.5
Neoprene	1.46
SBR	1.43
Nitrile (Hycar 1001)	1.39
Butyl (GR-I)	1.34

ing butyl, available from the literature. These data are shown in Table XIII for decreasing order of the coefficient. According to Martin and Neu[58], the literature shows a spread of 1.39 to 1.67 for natural rubber and a spread of 1.47 to 1.59 for SBR. The coefficients for these two polymers, at least, appear to be dependent on the nature of the vulcanizing system used. In contrast to this, Martin and Neu found that, with one exception, the coefficient for butyl was constant at about 1.37 for a number of vulcanizing systems including the quinoid. The zinc and cadmium salts of diethyldithiocarbamic acid gave appreciably higher coefficients around 1.55.

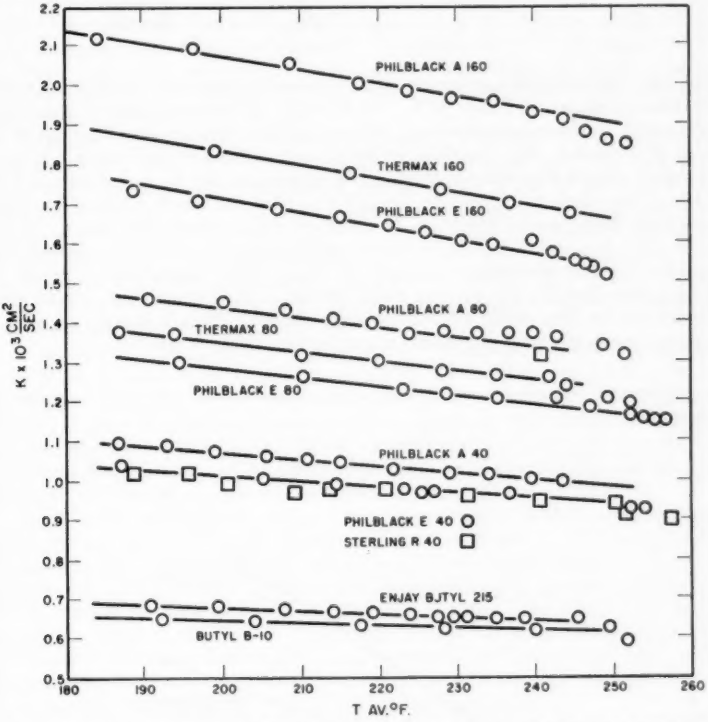


FIG. 37.—Black fillers—thermal diffusivity versus mean temperature (MacRae and Zapp[44]).

The importance of this work is that a low temperature coefficient leads to practical difficulties at both ends of the temperature scale of use. At the lower temperature range, a low coefficient mirrors rapid reaction rates leading to "scorch." At higher temperature ranges, where speed of reaction is desired, the reaction time will be longer than desired. The data obtained on the zinc and cadmium salts of the thiocarbamic acid should lead to a more tractable temperature situation for butyl polymers in actual practice.

Gordon[59] using the data of Zapp and coworkers, calculated the reaction rate constants at three temperatures for the vulcanizing systems of sulfur with

TABLE XIV

UNIMOLECULAR RATE CONSTANTS FOR VULCANIZATION OF BUTYL WITH TELLURIUM DIETHYLDITHIOCARBAMATE AND SULFUR AND TETRAMETHYLTHIURAM DISULFIDE AND SULFUR (GORDON[59])

Vulcanizing system	Temperature, °F	Unimolecular rate constant, k
TDEDC—Sulfur	250	0.00221
	300	0.0135
	400	0.3700
TMTDS—Sulfur	250	0.0010
	300	0.0150
	400	0.3000

tellurium diethyldithiocarbamate and tetramethylthiuram disulfide in butyl. His data are shown in Table XIV. Plots of rate of disappearance of free sulfur led Gordon to the conclusion that, for most of the vulcanization time up to the onset of reversion, the reactions of butyl and sulfur are first order. Gordon suggested that a slow step involving the opening of the S_8 ring controlled the order of the reaction. However, Craig[60] feels that the reaction is not first order since then butyl would vulcanize at the same rate as other elastomers. A plot of the same data used by Gordon (shown previously in Table VIII) relating combination of sulfur with time was made by Craig and is reproduced in Figure 38. Craig argues that for the greater period of the vulcanization time, a zero order dependence on free sulfur concentration is shown. This is clearly an area of research, basic to butyl polymers, where further effort is needed.

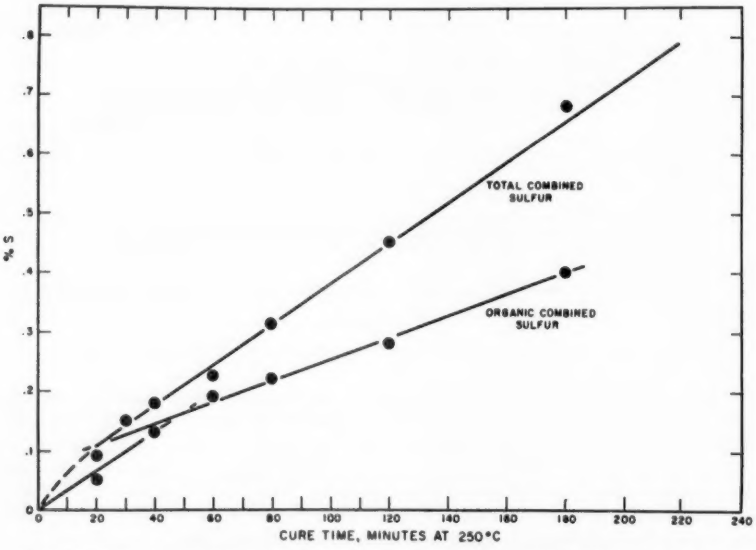


FIG. 38.—Sulfur combination for butyl from data of Zapp. Vulcanizate contained: polymer—100 (0.0758 mole of double bonds), zinc oxide—5, tellurium diethyldithiocarbamate—1.55, and sulfur—2 (0.0625 atom of sulfur) (Craig[60]).

VII. RESPONSE TO DEFORMATION

The elastic response of elastomers to deformation is their most important technical property. It is this property that characterizes their usefulness in applications where relatively high but elastic deformation is required under light forces without rupture or failure to the rubber part. All elastomers, being composed of long chains with internal mobility display this property. The internal mobility allows the necessary rearrangements of chain configurations during the deformation process and the retraction or recovery process. Although all elastomers satisfy these requirements for elasticity, it is apparent that there are major differences. These differences arise largely from factors controlling the number of configurations allowed to the polymer chains when a force is applied and after it is released. It follows from the discussion on the structure of polyisobutylene and butyl polymers that there are distinct factors in these chains which will have a major effect on the nature of the elastomeric response in deformation.

In order to have a reasonable level of elastic behavior, it follows that the polymer chains must be restricted in their tendency to slip past each other while under strain, and thus exhibit plastic flow. Thus, a permanency of structure is required for high level elasticity and this in turn demands the existence of a network of the chains. It is true that the relative plastic and elastic response to deformation is important to rheology and associated processes. Some attention has already been given to this field earlier in this review. The intention here is to deal with crosslinked networks and the factors concerned with their elasticity.

A simplified approach to a discussion of elasticity in butyl vulcanizates could involve three areas: (1) the stress-strain curve under ordinary conditions, (2) stress relationships under equilibrium conditions and (3) dynamic behavior. A good deal of attention has already been given in this review to the first approach listed. It is true that further enlightenment on the behavior of butyl in deformation processes could result from analysis of simple stress-strain data. However, the attention here will be given to the other two areas.

Equilibrium stress-strain.—The value of experimental data from stress-strain experiments where the sample is at equilibrium conditions is, of course, a result of simplification of analysis due to minimization of time effects. Thus, the analysis can take up the contributions of the permanent network restraints as major controlling factors in the deformation process. Such experiments are immensely useful in studies of crosslinked structure, vulcanization, reinforcement and degradation processes. It is recognized, of course, that the equilibrium method can employ both mechanical strain and the extension of the network through the swelling action of appropriate solvents.

Experimental examination of statistical theory of rubber elasticity.—James and Guth[61] set forth a theory of rubber elasticity in terms of the stress as a function of extension, the temperature and the pressure.

$$Z = KT\left[L - \frac{V\,(LTP)}{L^2}\right] \tag{1}$$

where $Z = F/A_0$, force per original cross-sectional area is the nominal stress, $L = l/l_0$, is the stretched length relative to the unstretched length and $V = v/v_0$, the volume of the stretched sample relative to the volume of the unstretched sample, T is the absolute temperature and P is the hydrostatic pressure of the medium surrounding the specimen.

Although numerous investigators had considered the stress-strain and stress-temperature relations of elastomers, no adequate test of the predictions of the theory was possible because of lack of precision particularly in the region of low extensions. Baldwin, Ivory and Anthony[62] studied this problem and provided data from research where careful attention was paid to the experimental details.

It can be shown, as these authors point out, that the total stress is the sum of the contributions of the entropy, Z_s, and the enthalpy, Z_h.

$$Z_s = KT\left[L - \frac{1 + \alpha\,(T - T_0)}{L^2}\right] - \frac{KT^2\alpha}{L^2} \tag{2}$$

$$= KT\left[L - \frac{1 + \alpha\,(2T - T_0)}{L^2}\right] \tag{3}$$

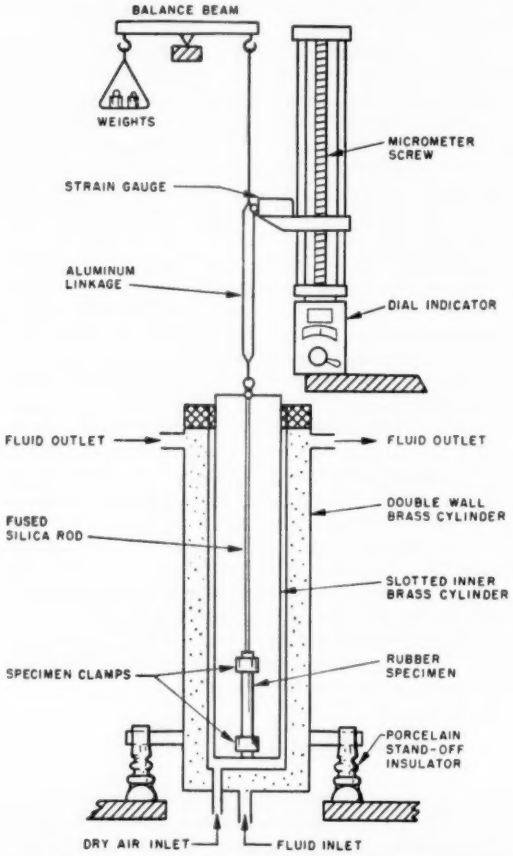


FIG. 39.—Schematic diagram showing main features of apparatus (Baldwin, Ivory, and Anthony[62]).

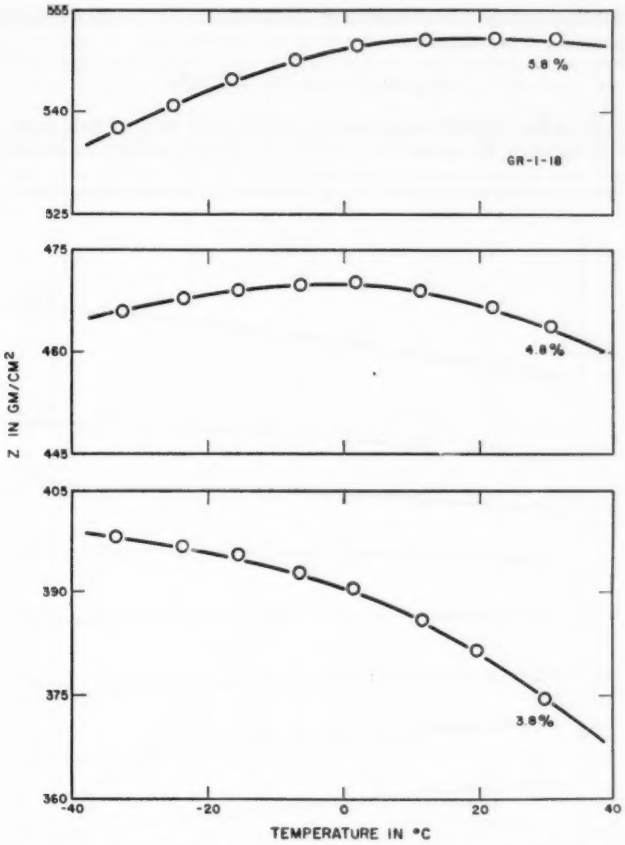


FIG. 40.—Stress-temperature behavior of GR-I-18 for three selected values of percentage extension (Baldwin, Ivory, and Anthony[42]).

and

$$Z_h = \frac{KT^2\alpha}{L^2} \tag{4}$$

The total stress may be written

$$Z = Z_s + Z_h = KT\left[L - \frac{1 + \alpha\,(T - T_0)}{L^2}\right] \tag{5}$$

where Z is the stress of the original theoretical expression in Equation (1) and α is the volume coefficient of thermal expansion. These expressions are of interest in that they predict two effects not observed in earlier less precise work. Equation (5) predicts a nonlinear dependence of Z on T, at constant specimen length. Equation (3) predicts that the thermoelastic inversion (the extension

for which the entropy contribution to stress is zero, $Z_e = 0$) should increase with increasing temperature.

$$L_{inv} = [1 + \alpha (2T - T_0)]^{\frac{1}{2}}$$

In view of the need for experimental precision in work of this type, it is of interest to consider the apparatus employed by these authors in obtaining the

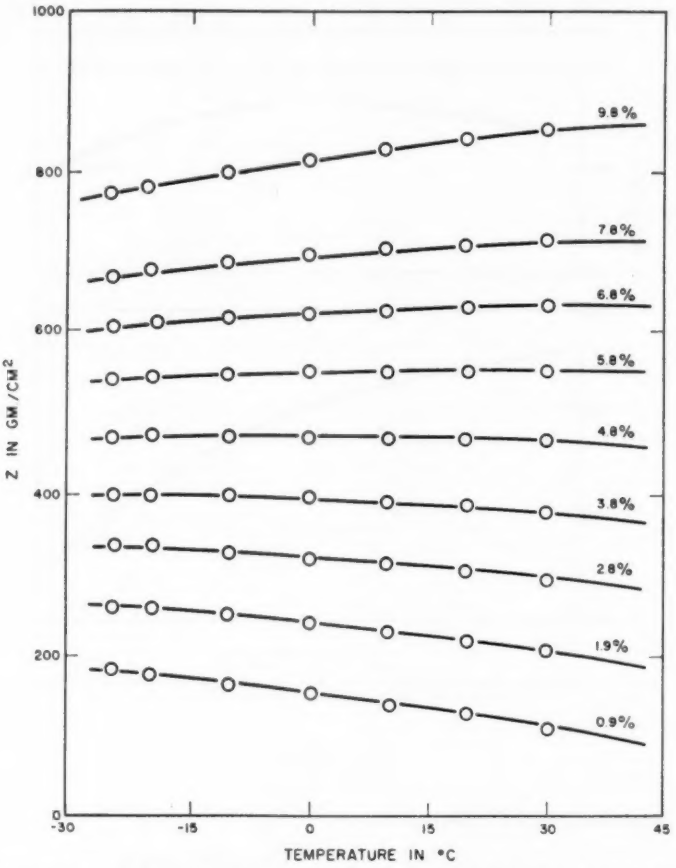


FIG. 41.—Family of stress-temperature curves for GR-I-18 (Baldwin, Ivory, and Anthony[61]).

required equilibrium stress-strain curves. A schematic diagram showing the main features of their apparatus is given in Figure 39. The apparatus has two essential features: (1) a force sensing system consisting of a fixed position strain gage (null indicator) in combination with a balance beam, and (2) constructional materials and details of assembly to insure that the sensing device

reflects the changes in the length of the sample with a minimum of interference from expansions or contractions due to the apparatus.

A series of stress-temperature plots at several low extensions as obtained by these authors is given in Figure 40. The sample employed was a pure gum vulcanizate of GR-I-18 (now Enjay Butyl 218). It may be noted that: (1) the dependence of stress on temperature is nonlinear, and (2) the thermoelastic

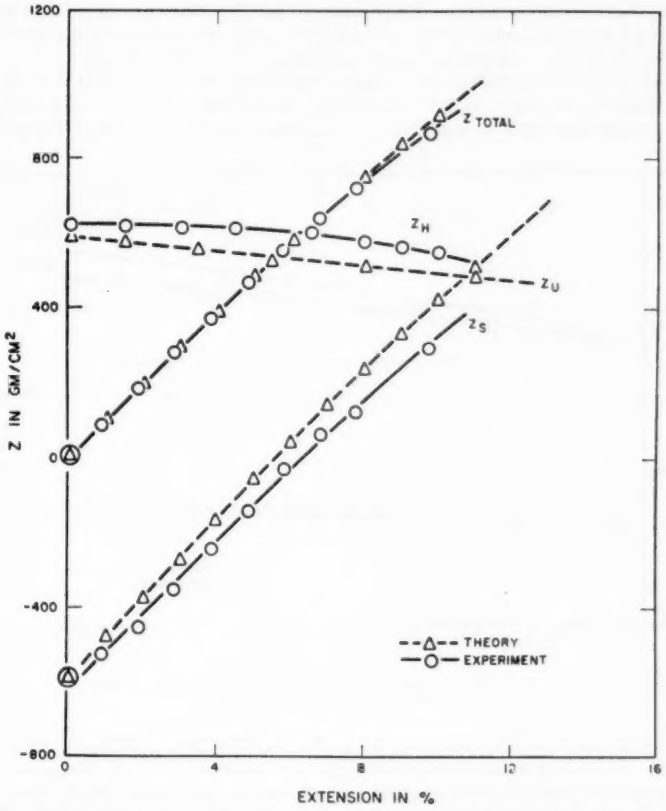


FIG. 42.—Theory versus experiment for GR-I-18 at 40° C showing the total stress Z, the enthalpy component $Z_H \simeq Z_U$, and the entropy component Z_S as functions of the percentage extension (Baldwin, Ivory, and Anthony[69]).

inversion temperature is shifted to higher values at higher extensions. Both of these results are in keeping with the predictions of the theory.

A family of stress-temperature curves over a wider range of extensions is given in Figure 41. These data provide the basis for the plot of theory versus experiment in Figure 42 where the stress is given as the total stress, and the enthalpy and entropy contributions to stress as functions of extension. It may be noted that there is good agreement between the actual data and the

theory. However, there would appear to be significant deviations from the predictions of the theory.

A further test of the theory relative to the temperature dependence of stress in the extension range 5.8–9.8% is given in Figure 43. Again, it may be noted that there is good agreement. However, once again there would appear to be deviations from the theory. These authors concluded that their experimental techniques were such as to allow the conclusion that the differences shown for both dependencies (extension and temperature) are real. The probability of intermolecular forces not included in the theory as being responsible for the deviations was offered as an explanation by these authors.

Elasticity and reinforcement.—Zapp and Guth[63] have presented data on the crosslinked networks in butyl vulcanizates using both volume swell techniques and equilibrium elastic modulus as evaluation tools. The main purpose of

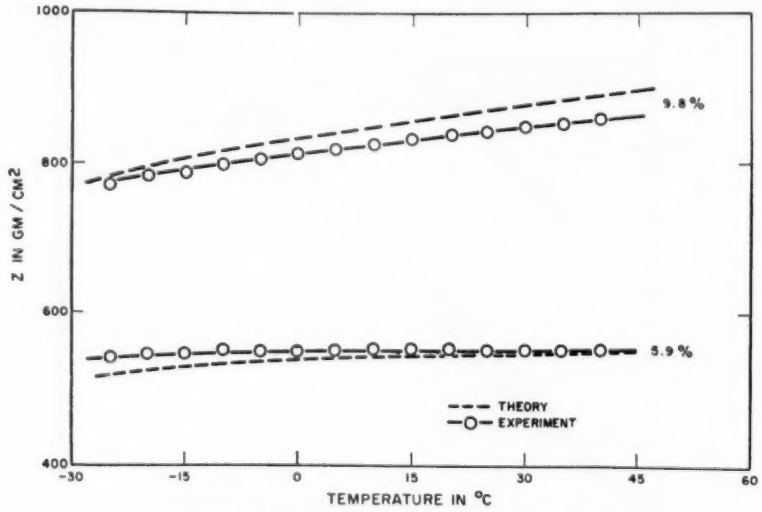


FIG. 43.—Theory versus observed temperature dependence of stress (Baldwin, Ivory, and Anthony[62]).

this work was to study reinforcement with carbon black and certain mineral fillers. They found that carbon black gave reinforcement to the butyl network in terms of a reduced volume swell and increased equilibrium elastic modulus. Mineral fillers failed to provide any reinforcement. From this work, it was concluded that carbon black reinforced butyl in relation to the available surface of the black. The higher the available surface, the higher was the reinforcement.

An interesting approach to the definition of the reality of reinforcement was employed by these authors. They first determined by means of an equilibrium elastic modulus technique that fillers, both carbon black and mineral types, give rise to higher equilibrium stress values at a given extension as a function of volume filler loading. Data of this type are shown in Figure 44 where it may be noted that the effect on stress as a function of filler loading is greater for the materials normally associated with reinforcement.

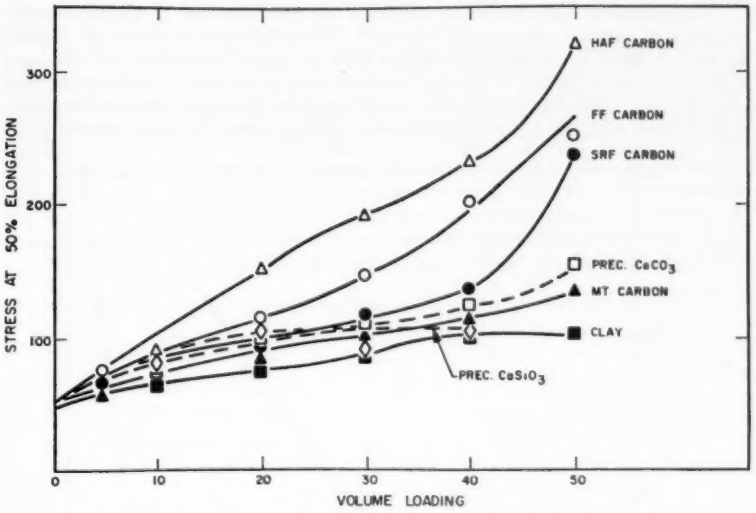


FIG. 44.—Equilibrium modulus as function of filler loadings (Zapp and Guth[43]).

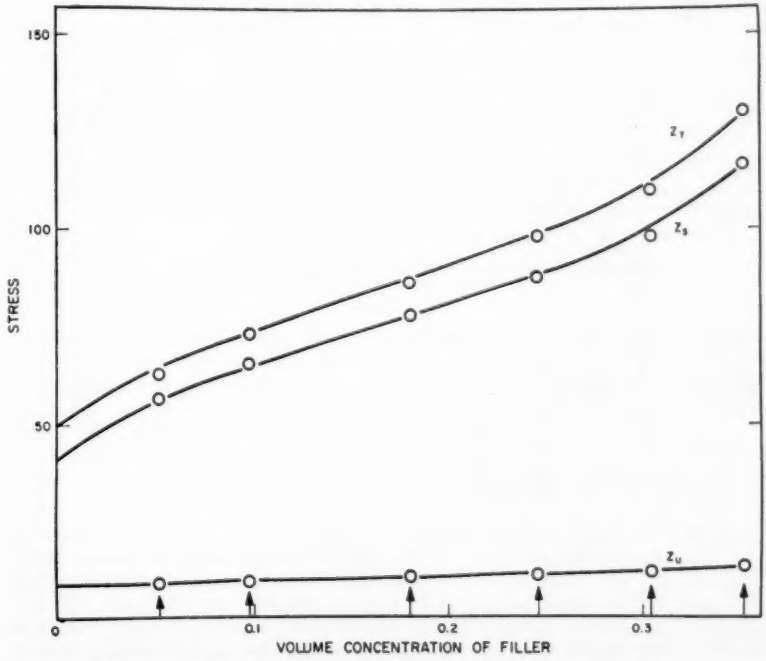


FIG. 45.—Medium thermal carbon contributions to stress (Zapp and Guth[43]).

These authors considered the nature of the contributions to the total stress in terms of entropy and internal energy. The relationships shown in Figures 45 and 46 serve to bracket the results they obtained for systems of "low and high reinforcing capacity". It may be noted that in the case of medium thermal carbon black, the increase in total stress is made up principally from the entropy contribution with the contribution due to internal energy changing only slightly

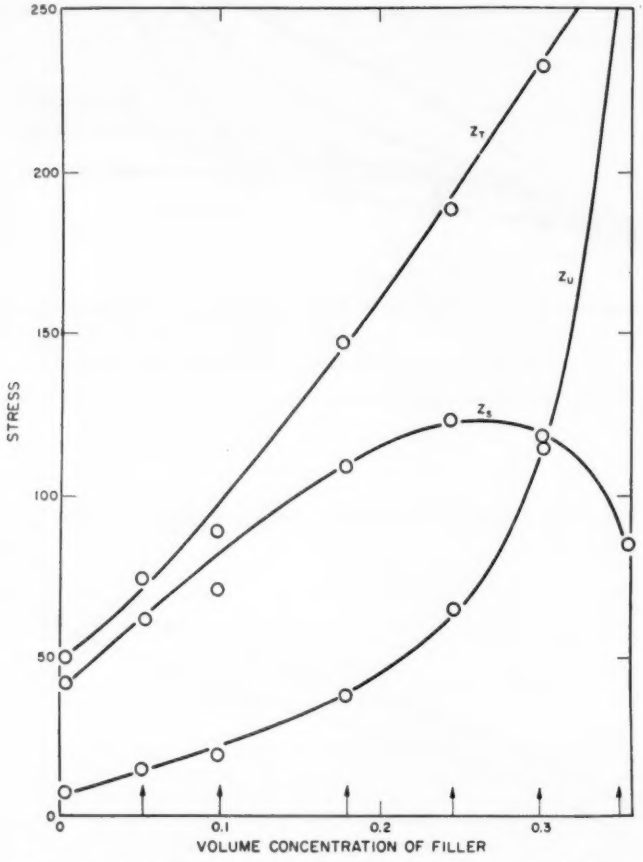


FIG. 46.—High abrasion furnace carbon contributions to stress (Zapp and Guth[48]).

with increased carbon black loading. Roughly similar effects were observed for the mineral filler systems. In the case of a high abrasion furnace black, both entropy and internal energy contribute to the increase of total stress with increased carbon black loading up to a given volume. At this point, the contribution of entropy decays and the contribution of internal energy increases rapidly with further loading. Other blacks such as semireinforcing furnace

and fine furnace fall intermediate between the two blacks discussed in the volume loading effects on the nature of the stress.

Although these results are instructive in assisting an understanding of reinforcement, it should be noted that a number of limitations must be recognized before broad interpretations are made. First, the extension used in these experiments was 50 per cent. This would appear to be relatively high to allow free application of the statistical theory of elasticity. Second, the strong tendency of the internal energy to increase with carbon black loading suggests that a type of particle-particle-polymer structure is being built up. This is consistent with the observation that the increase in internal energy contribution to stress is dependent on the total surface of carbon black added as shown in Figure 47. Carbon blacks with high surface-volume ratios are believed to prefer

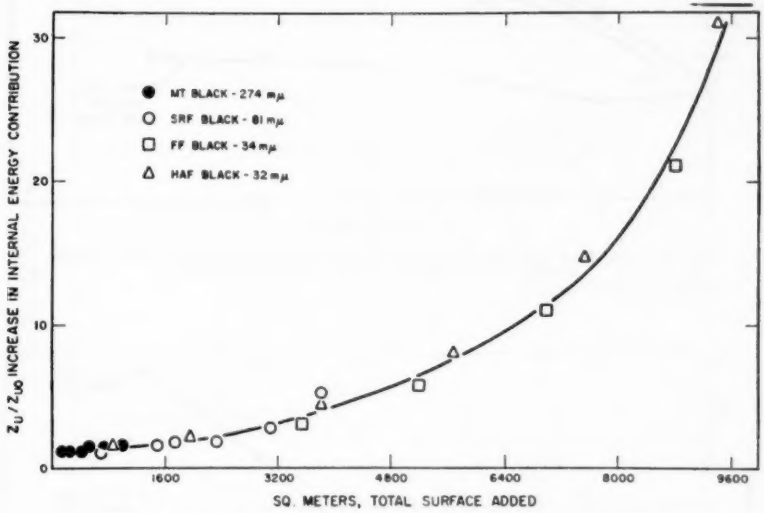


FIG. 47.—Increase in internal energy contribution as function of total surface of carbon black added (Zapp and Guth[69]).

association with themselves. Third, the addition of a foreign material results in a dilution of the polymer in the sample. The number of points of restraint or the actual polymer chain length between points of restraint can be affected. Thus, for a given macro-extension, the average chain may on a micro scale be under very high strain.

A further test of the reality or permanence of reinforcement was made by these authors. They compared the contribution of a semi-reinforcing carbon black (with an average particle diameter of 81 millimicrons) and precipitated calcium carbonate (with an average particle diameter of 87 millimicrons) to equilibrium elastic modulus in the swollen and unswollen states. In order to make the comparison, it was necessary to recognize that the swollen samples represent a certain state of elongation of the chains and this requires a compensation. Their comparison of the two systems of filler, in the swollen and unswollen (compensated) states are given in Figures 48 and 49. It is shown that

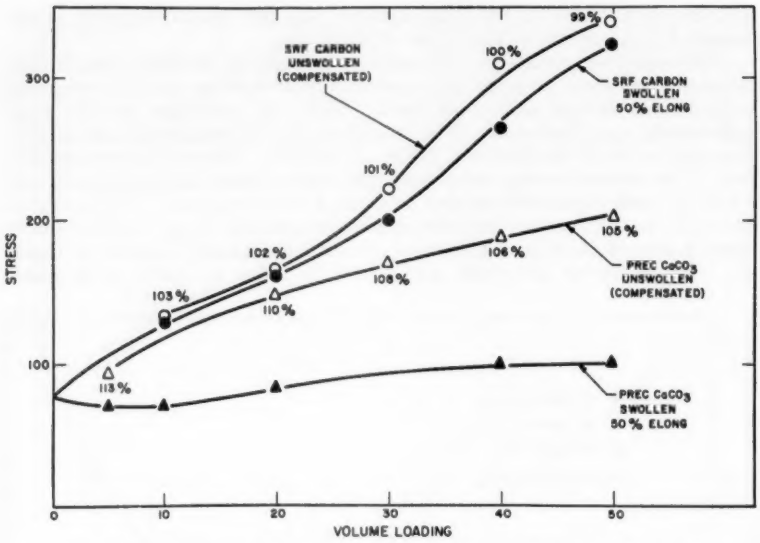


FIG. 48.—Comparison of swollen equilibrium modulus at 50 per cent extension with unswollen specimens of compensated extension (Zapp and Guth[42]).

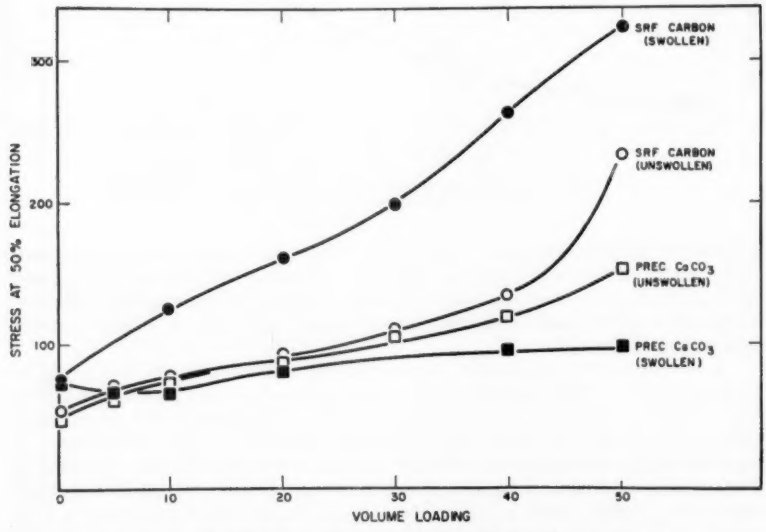


FIG. 49.—Comparison of equilibrium modulus at 25° C of swollen and unswollen networks at same extension (Zapp and Guth[42]).

the carbon black system maintains its contribution to the elastic stress even in the swollen state while the calcium carbonate system does not. On the basis of these data, they considered the well-known problem of whether fillers actually reinforce a polymer chain structure with relatively strong bonds and whether there is any real differences in this regard in the case of carbon blacks and mineral fillers. These authors concluded that the carbon black had imparted an additional restriction in the form of a type of cross-linking very likely due to the activity of its surface. It was concluded that mineral fillers are incapable of this type of reinforcement.

Boonstra and Dannenberg[64] presented data on the swelling of a number of polymers and pigment systems in a variety of solvents. These authors show examples where on the basis of reduced volume swell it might be concluded that

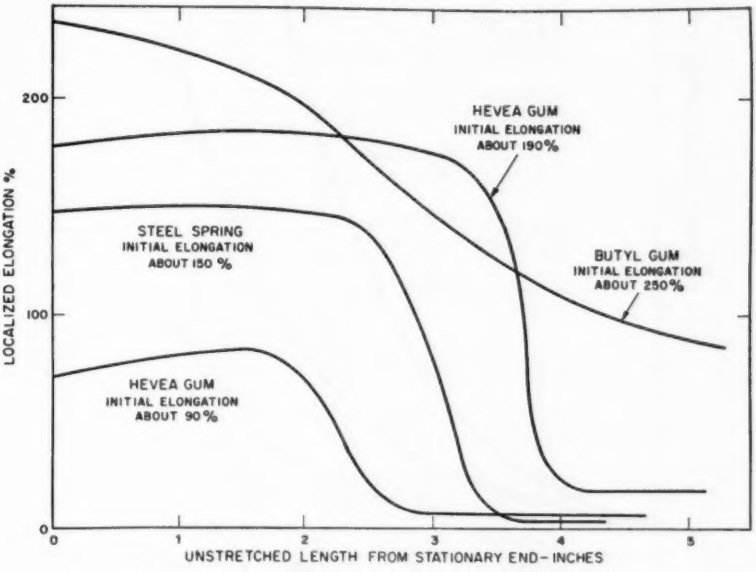


FIG. 50.—Local elongation versus unstretched length (Stambaugh[64]).

a butyl-clay vulcanizate would appear about as well reinforced by the presence of clay as a natural rubber-channel black vulcanizate is reinforced by the presence of the carbon black. There is considerable practical evidence that this is not the case. The treatment of Zapp and Guth assists in clarifying such a comparison.

Dynamic behavior.—A knowledge of the dynamic behavior of elastomers is of importance for both purposes of application and inquiry into polymer and compositional effects on elasticity. An excellent and extensive review of dynamic measurements and their significance has been made by Gehman[65]. This review contains numerous references to butyl vulcanizates.

It was early recognized that the chain structure of butyl polymers would give rise to hindered motion. Thus, for a given force stored in a stretched

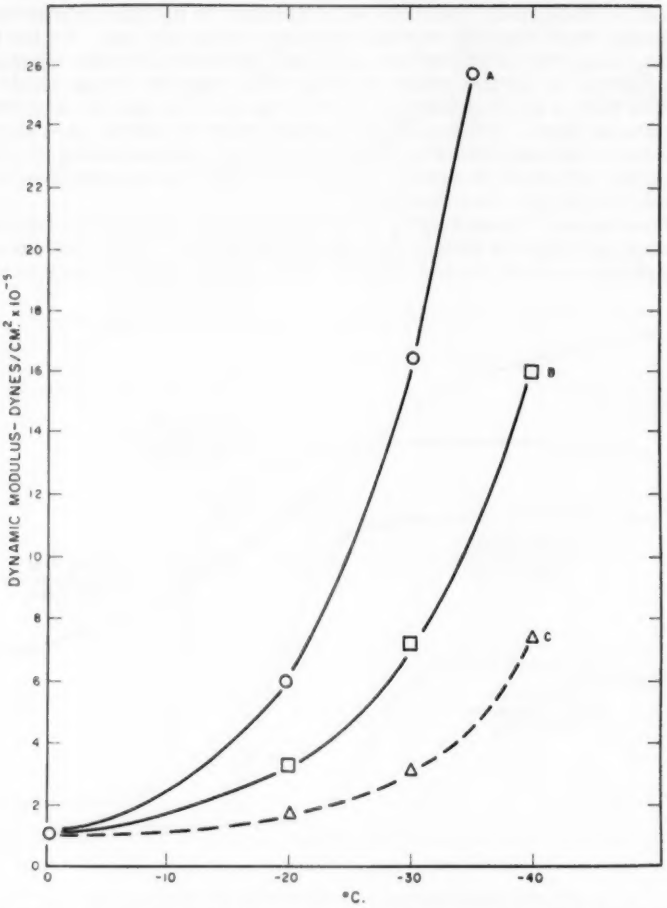


FIG. 51.—Dynamic modulus of butyl vulcanizate with 25 phr of hydrocarbon oil (A), 25 phr of di-octyl sebacate (B) and natural rubber vulcanizate with 5 phr of hydrocarbon oil (C).

sample, a slower retraction would be observed than in the case of less hindered samples. The relative retractive speeds of butyl and natural rubber vulcanizates have been observed by Stambaugh[66]. The retraction speeds and the nature of the retraction were measured by an interrupted light beam-photocell technique and these measurements were verified by high speed photographs. A plot of these data is shown in Figure 50. The systems of low internal friction show a wave front form of retraction while butyl shows no wave front but a progressively lower elongation along the stretched sample as retraction progresses.

Dillon, Prettyman and Hall[67] compared the hysteretic and elastic properties

TABLE XV

DYNAMIC PROPERTIES OF VARIOUS RUBBERS

Maximum driving shear stress = 34,500 dynes per sq cm; frequency = 60 cycles per second; static compressive strain = 0.15 (Dillon et al.[67])

Stock type	Base rubber	$\omega\eta(aHe)$ (megagrams/cm/sec²)			G (megadynes/cm²)			G_{tt} (megadynes/cm²)			β (dimensionless)			H_σ (relative to hevea tread at 50° C)		
		30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100°C
Gum	Hevea	0.270	0.205	0.132	3.08	2.97	3.09	2.53	2.56	2.72	0.088	0.080	0.043	533	450	266
	SBR	0.958	0.734	0.417	5.29	4.43	3.74	2.67	2.56	2.72	0.181	0.165	0.111	642	720	573
	Butaprene-NM	2.295	1.048	0.696	9.43	7.92	6.86	4.82	4.23	4.98	0.243	0.132	0.101	459	320	284
	Neoprene-GN	1.01	0.700	0.682	6.21	5.24	4.59	3.31	2.61	2.20	0.163	0.134	0.149	496	496	620
	GR-I	2.49	0.765	0.250	4.11	3.17	2.56	2.29	2.21	2.21	0.607	0.241	0.113	2390	1430	718
Tread	Hevea	3.02	1.92	1.07	24.0	19.2	13.9	17.9	17.1	12.8	0.126	0.100	0.077	95	100	106
	SBR	8.76	6.74	3.04	53.8	41.1	17.4	25.1	18.3	9.9	0.163	0.164	0.174	56	76	191
	Butaprene-NM	5.10	3.06	1.48	27.3	20.1	13.2	14.6	11.6	9.9	0.187	0.144	0.112	126	132	162
	Neoprene-GN	5.00	2.78	2.02	26.5	20.8	17.7	13.8	12.8	10.6	0.188	0.133	0.114	130	123	124
	GR-I	14.60	7.55	2.02	34.9	28.5	13.3	18.1	14.2	8.5	0.412	0.265	0.152	232	176	217

of various elastomers under dynamic shear stresses using a resonance shear vibrator. A summary of their data for gum and tread type vulcanizates is given in Table XV. The notations used as headings of the five columns may be broadly defined as follows.

$\omega\eta(\alpha H\epsilon)$ = absolute damping, hysteresis loss per cycle in unit volume at constant maximum strain.

G = dynamic modulus

G_{st} = static modulus

g = dimensionless constant = $\omega\eta(G)$

H_σ = hysteresis loss per cycle in unit volume at constant maximum stress.

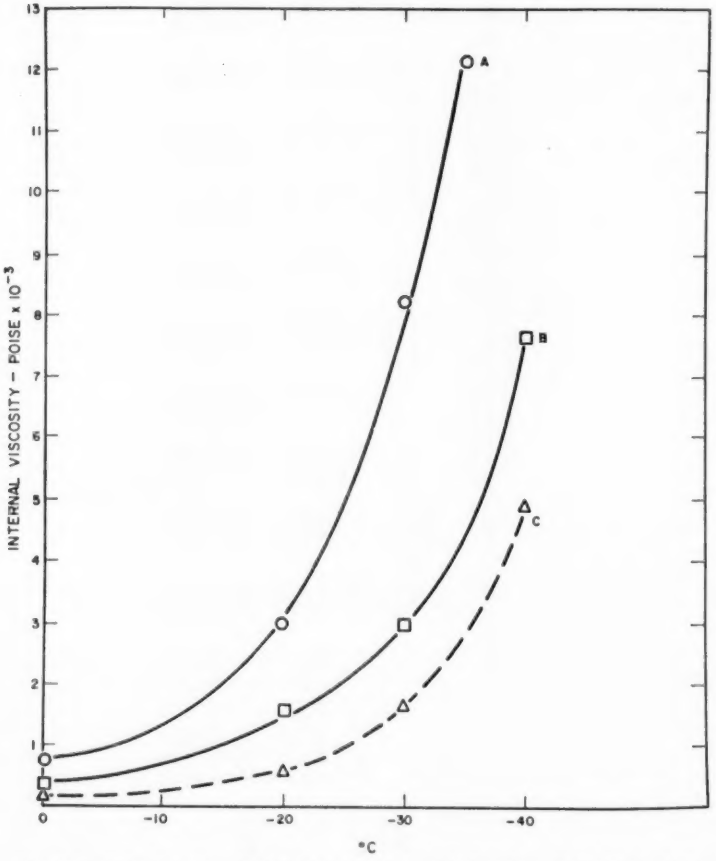


FIG. 52.—Internal viscosity of butyl vulcanizate with 25 phr of hydrocarbon oil (A), 25 phr of di-octyl sebacate (B) and natural rubber vulcanizate with 5 phr of hydrocarbon oil (C).

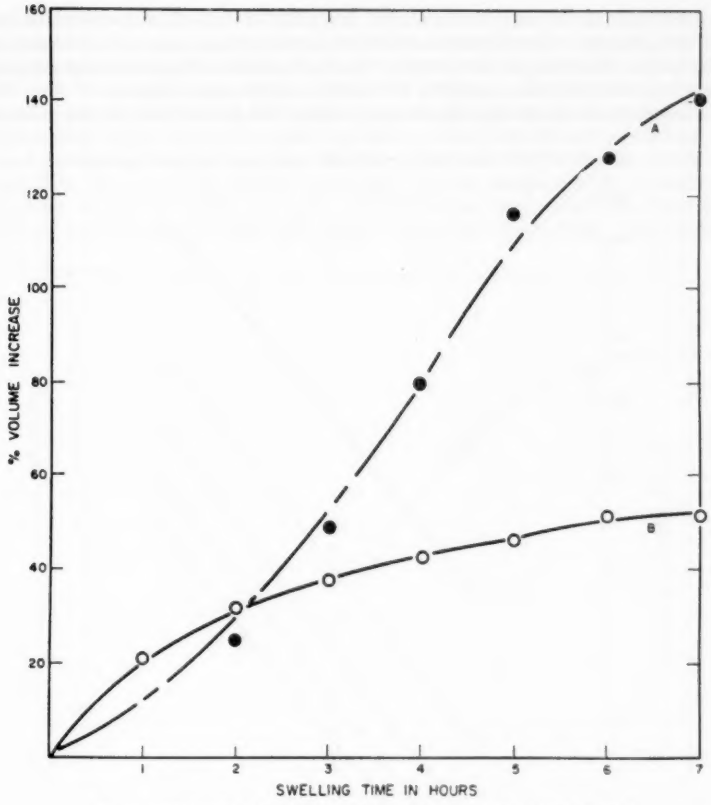


FIG. 53.—Swelling of a butyl vulcanizate in hydrocarbon oil (A) and di-octyl sebacate (B) at 0° C.

It will be noted that the butyl vulcanizates (referred to as GR-I) have higher damping and this is more pronounced at lower temperatures.

Plasticizers.—As part of the growing knowledge on butyl vulcanizates, it became apparent that the internal friction could be reduced by use of proper plasticizers to a point entirely suitable for many uses[68]. Hydrocarbon oils of moderate viscosity have been found very useful in this regard. Data showing the relative behavior of a hydrocarbon oil plasticizer and an ester (dioctyl sebacate) on the internal viscosity and dynamic modulus of a butyl vulcanizate at extreme low temperatures are shown in Figures 51 and 52. A comparison is made with a natural rubber vulcanizate. The method used for the dynamic measurements was the free vibration method of Baldwin[69].

The plasticizing action of a plasticizer should be dependent on two factors: (1) the solubility characteristics of the plasticizer-polymer system and (2) the viscosity-temperature properties of the plasticizer. The first factor controls the ability of the plasticizer to separate polymer chains and reduce hindered

motion and the second controls the mobility of the plasticizer within the rubber network. The importance of the second factor is apparent in the data of Figure 53. Here the solvent power of the hydrocarbon oil and di-octyl sebacate are compared in terms of ability to swell the butyl vulcanizate at 0° C. The hydrocarbon oil shows greater swelling action but its mobility in the network

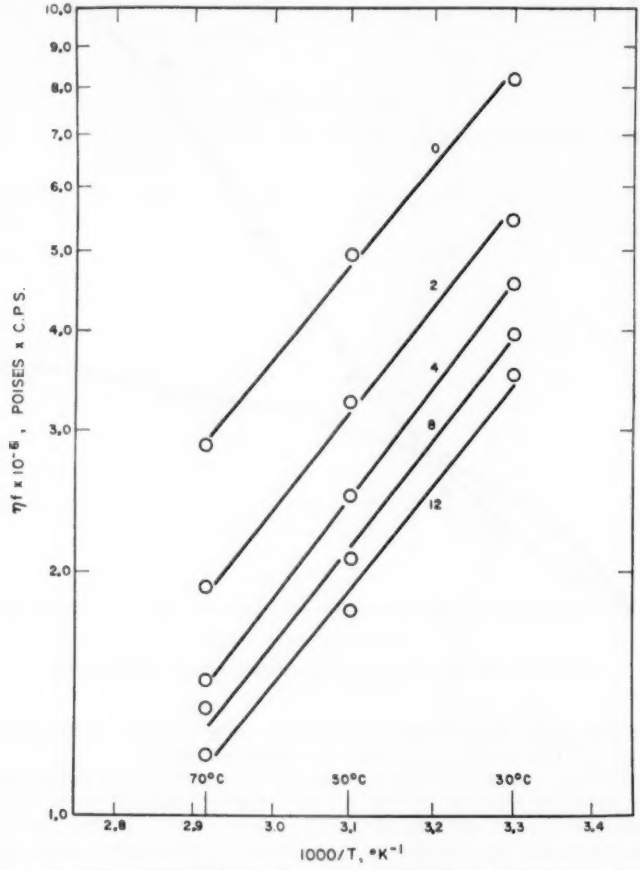


FIG. 54.—Effect of heat treatment on damping properties of butyl. The figures refer to the number of cyclic heat treatments (Gessler[71]).

would be much less as judged by the results on internal viscosity and dynamic modulus over the low temperature range.

Carbon blacks and heat treatment relative to dynamic behavior.—It is well known that the presence of solid foreign bodies in elastomer networks can materially affect hysteretic properties. Gehman, Woodford and Stambaugh[70] observed that an eight-fold increase in the internal friction of a natural rubber

vulcanizate results from the addition of 20 volumes of a gas black to a pure gum compound. Recognizing this profound effect, Gessler[71] undertook the study of polymer-pigment habit and in a series of experiments made an important contribution to the field of polymers and filler systems. He showed that when butyl was subjected to the shearing action of milling in the presence of carbon blacks with active surfaces material reduction in the contribution of the carbon black to internal friction could be effected. Together with Ford[72], it was shown that this effect could be greatly accelerated by the presence of paradinitrosobenzene during the milling process. Further work by Robison, Baldwin and Fusco[73] developed more highly efficient promoters for this process. An eventual

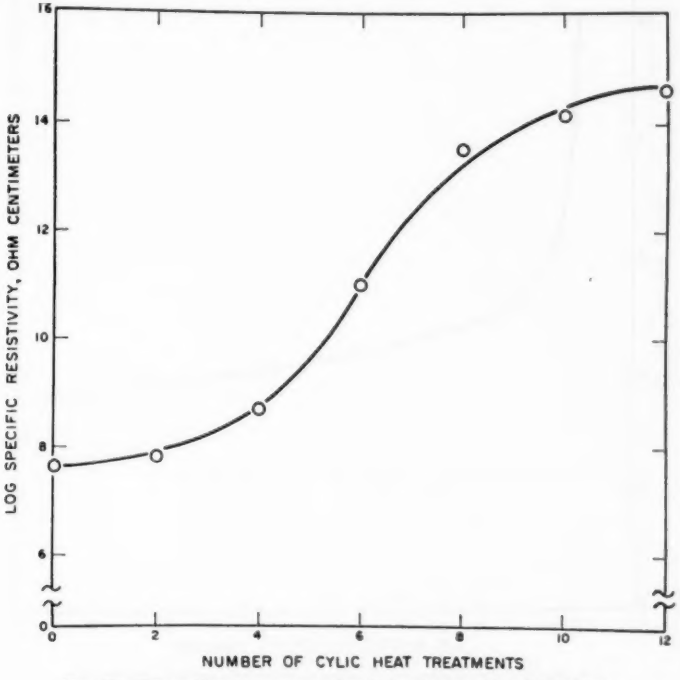


FIG. 55.—Effect of heat treament on electrical resistivity of butyl (Gessler[71]).

outcome of this work was the development of N-methyl-N,4-dinitrosoaniline as a heat treatment promoter of butyl and carbon black mixtures. An excellent treatment of the effectiveness of this material in butyl is given by Leeper and associates[74]. The effectiveness of heat treatment with the promotional aid of nitroso compounds on the quality of butyl tires is reviewed by Buckley[75]. Here it is shown that the general durability of butyl tires on severe overload and high speed wheel tests is greatly improved with the accelerated heat treatment systems. Almost invariably, this improvement is consistent with a major decrease in the heat build-up tendencies of the butyl vulcanizates in question. In view of the major importance of this work in reference to butyl and polymer-

pigment systems, further consideration will now be given to the evolution of this research.

Gessler observed that repetitive heating and shearing of a mixture of butyl and carbon black produced a desirable change in the absolute damping of the resultant vulcanizates. His data relating the absolute damping to extent of milling are shown in Figure 54. In this plot, the absolute damping expressed as the product of viscosity and frequency in a free vibration system is related to the temperature of the test for a number of "cycles" of milling. Each cycle represents 30 minutes exposure to a temperature of 320° F (open steam) fol-

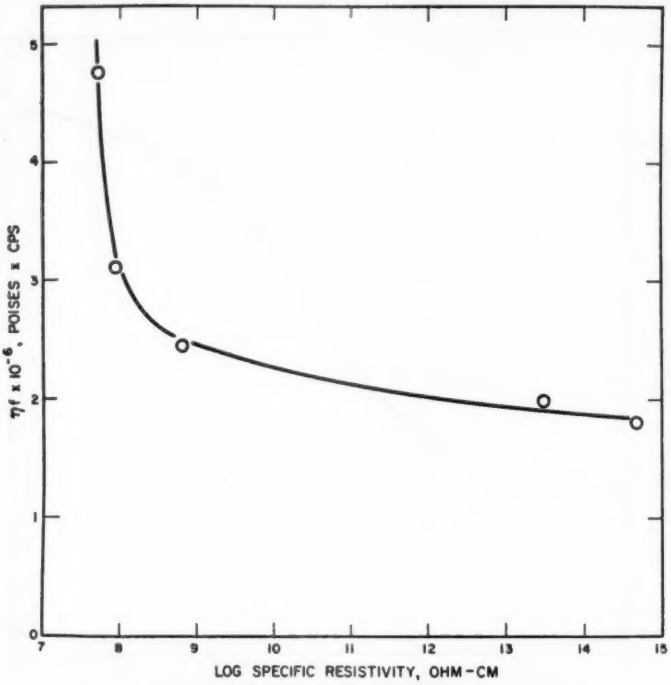


FIG. 56.—Relation of absolute damping to changes in electrical resistivity achieved through heat treatment process.

lowed by 5 minutes of milling (cool). It was reasoned that the process had resulted in a more discrete distribution of the carbon particles and the average interference with chain mobility in the vibration experiment had been reduced. Electrical resistivity measurements made on corresponding vulcanizates furnished the data shown in Figure 55. If the resistivity is, as generally believed, taken as a reliable measure of the separation of the more highly conductive black agglomerates into the more discrete particles more uniformly spaced and isolated by the less conductive polymer, then an interesting observation can be made in this process. Plotting the absolute damping as a function of the resistivity as shown in Figure 56 gives some clues as to the possible mech-

anism. It is found that with minor changes in the resistivity, and thus the degree of dispersion, large changes in the absolute damping are observed. This could mean that the agglomerates in butyl-carbon black mixtures are originally very large in the sense of forming a type of chain structure of their own running through the matrix of polymer chains. These chains can form paths for the relatively high electrical conductance observed. Further, they could provide high interference to the mobility of the polymer chains. Moreover, the usefulness of the reactivity of the carbon black surface in reinforcement would be less because of the preferred interaction of particle surfaces with each other. Gessler reasoned that the cyclic heating-shearing technique first disrupts the

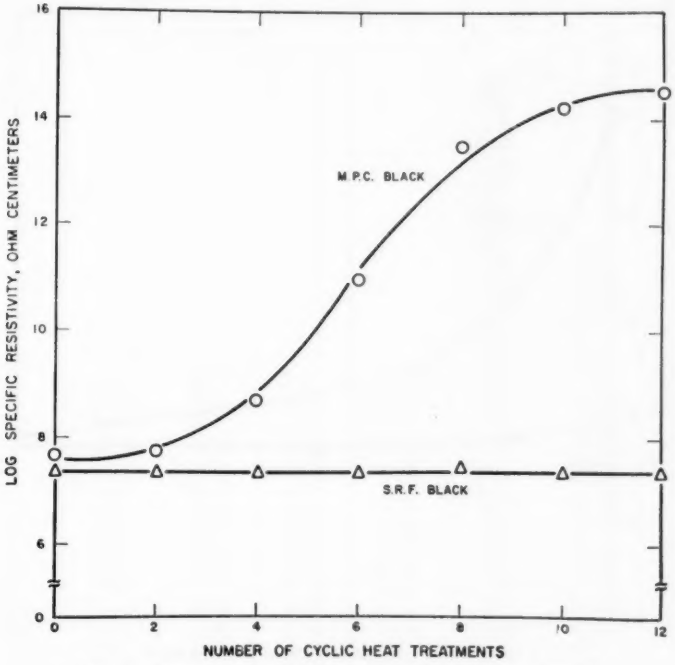


FIG. 57.—Dependence of heat treatment on carbon black type: electrical resistivity (Gessler[71]).

chains and with continued treatment makes available larger numbers of particles with free active surfaces for the reinforcement process. Some of his experiments supporting this view are shown in Figures 57 and 58. Here, two carbon blacks, a channel (MPC) and a semireinforcing black (SRF) were used. These two blacks are known to differ in their particle size and surface activity, the channel black being the smaller and the more highly oxygenated. It can be observed that in terms of dispersive effects of the heat treatment (as measured by the change in electrical resistivity) and the effects on the vulcanizate as noted in absolute damping, the channel black response is marked while the SRF appears unaffected.

Gessler further showed the necessity of supplying mechanical work to the system in order to realize the maximum effects. He compared the relative effects of static treatment (heating only) and the cyclic treatment (heating followed by shearing) on the change in electrical resistivity and absolute damping. It was observed that the effect of static treatment on the electrical resistivity was relatively small while there is a larger effect on the absolute damping. Large effects on both properties were observed for the cyclic treatment. This is consistent with the previous conclusion that rather pronounced effects relative to chain mobility would be obtained with the first disruption of particle-particle interactions. Further rupture of these interactions, in the cyclic proc-

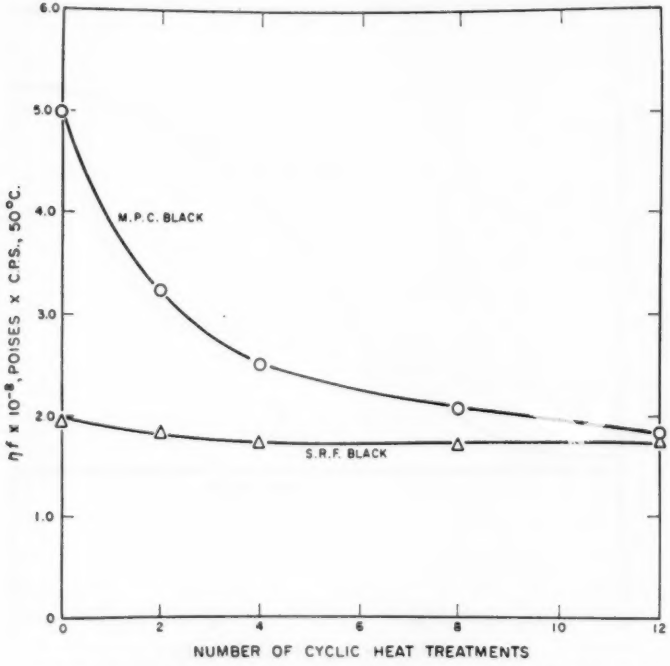


FIG. 58.—Dependence of heat treatment on carbon black type: damping (Gessler[71]).

ess, leads to continued increases in resistivity and reductions in the absolute damping.

Gessler and Ford showed that certain materials acted as promoters of the heat treatment process. The effects of sulfur as an aid in the process in terms of changes in electrical resistivity and absolute damping are shown in Figures 59 and 60. Some interesting departures with respect to the previously established relation between these two properties are noted for the range of carbon blacks employed and suggest a more complex system when a material reactive towards the polymer chain is employed. These authors investigated another material, also capable of showing reactivity towards the polymer chain, namely *p*-dinitro-

benzene. They found that this agent would produce the desired effect on reduction of absolute damping and increase of electrical resistivity. A comparison of heat treatment systems and their electrical resistivities against the number of heat treatment cycles is given in Table XVI. It is immediately apparent that the promoter, *p*-dinitrosobenzene, is very effective.

It was found further that *p*-dinitrosobenzene was effective in the presence of both MPC and SRF blacks. In addition, they developed the potential use of the promoted system for a commercial Banbury operation. It was also noted

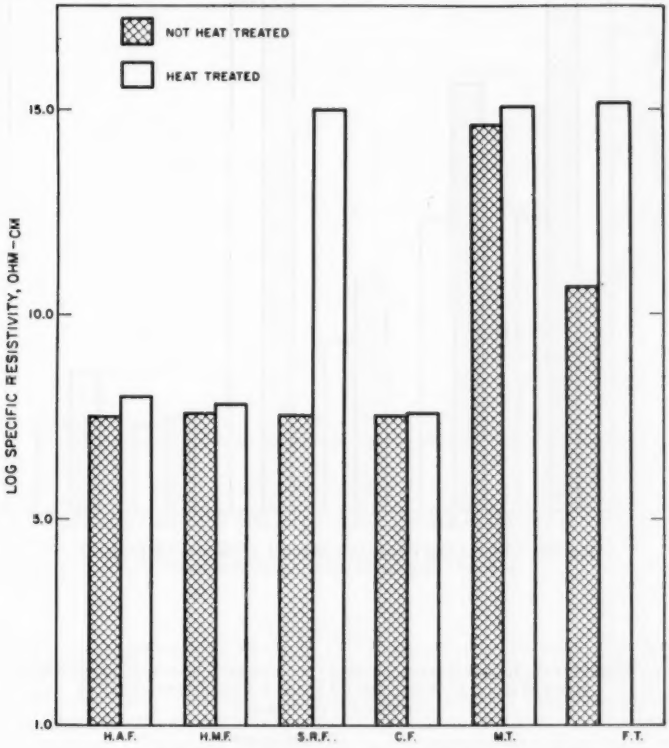


FIG. 59.—Effect of heat treatment with sulfur on the electrical resistivity of butyl with different blacks (Gessler and Ford[72]).

that the dinitrosobenzene appears capable of reducing the absolute damping to some extent in the absence of a "heat treatment". The authors suggest that some activity on the part of this agent during the vulcanization process is possible. It is of interest that *p*-dinitrosobenzene, at the concentrations used by these authors, is an extremely active cross-linking agent for butyl polymers. In this regard, it would be of importance to know whether crosslinking of the polymer, or reaction of one of the bifunctional units in dinitrosobenzene, plays a role in promotion of the heat treatment process.

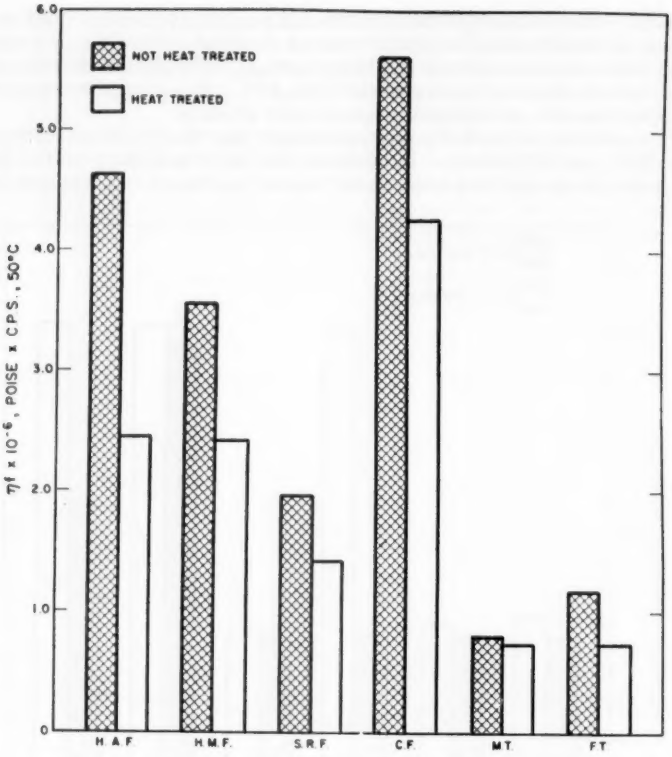


FIG. 60.—Effect of heat treatment with sulfur on the damping properties of butyl with different blacks (Gessler and Ford[72]).

TABLE XVI

ELECTRICAL RESISTIVITIES OF BUTYL–CHANNEL BLACK COMPOUNDS HEAT TREATED WITH AND WITHOUT PROMOTING AGENTS (GESSLER AND FORD[72])

Number of cyclic heat treatments	Promoting agent		
	Electrical resistivity, ohm cm.		
	None	Sulfur	Polyac
0	4.12×10^{7}	3.90×10^{7}	6.71×10^{10}
1	—	3.69×10^{7}	7.46×10^{14}
2	5.58×10^{7}	1.96×10^{9}	$>10^{15}$
3	—	3.41×10^{12}	$>10^{15}$
4	4.21×10^{8}	—	—
5	—	1.27×10^{14}	$>10^{15}$
6	9.32×10^{10}	—	—
8	3.22×10^{12}	$>10^{15}$	$>10^{15}$
10	1.46×10^{14}	—	—
12	3.22×10^{14}	$>10^{15}$	$>10^{15}$

The commercial development of the heat treatment process with carbon blacks reached a high point of usefulness in the butyl passenger tire. The work of Robison, Baldwin and Fusco in the application of *p*-nitrosophenol and N-methyl-N,4-dinitrosoaniline to tire compounds was reviewed in comparison with *p*-dinitrosobenzene by Buckley. The three structures for these compounds are shown in Figure 61.

These compounds present a number of similarities and a number of dissimilarities with regard to polymer-pigment interactions considered attributable to heat treatment effects.

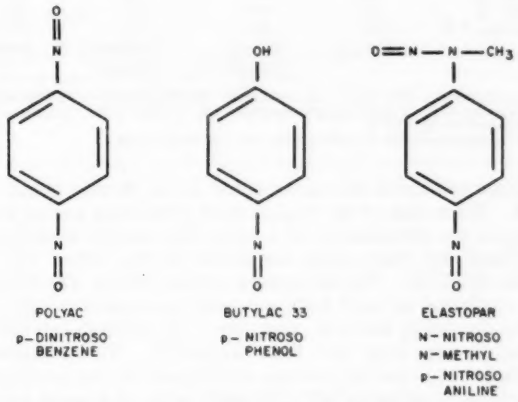


FIG. 61.—Chemical promoters for heat treatment of butyl compounds (Buckley[78]).

SIMILARITIES

1. All are bifunctional, nitroso compounds, para-substituted.
2. All produce, in some degree, the polymer-pigment interaction.
3. All are capable of crosslinking butyl polymers.

DISSIMILARITIES

1. They vary greatly in efficiency and effectiveness with "Polyac", the slowest, and "Elastopar", the fastest. Approximate times and temperature for interaction are: "Polyac", 10–15 minutes at 400° F, "Butylac-33", 8–10 minutes at 300° F and "Elastopar", 2–3 minutes at 280° F.
2. "Polyac" and "Elastopar" are effective in the presence of carbon black, while "Butylac-33" is only effective when pre-reacted with the polymer.
3. "Elastopar" is almost equally effective whether prereacted with polymer or added just before the carbon black.
4. "Elastopar" is by far the most effective in reducing internal friction of vulcanizates.

Polyac—product of E. I. duPont deNemours and Co., Inc.
Butylac-33—experimental product of American Cyanamid Co.
Elastopar—product of Monsanto Chemical Company

Elastopar has subsequently been used extensively in butyl passenger tire compounds. The main reason for this is reflected in the effect of this agent in

TABLE XVII

FLEXING BEHAVIOR. EFFECT OF "ELASTOPAR" CONCENTRATION (BUCKLEY[75])

"Elastopar"[a]	0	0.1	0.3	0.5	1.0
Forced vibration, 122° F—16 cps					
K, dynes/cm^2 $\times 10^{-7}$	2.58	2.52	2.18	2.22	2.10
Relative damping, %	46	44	40	35	34
η, poises $\times 10^{-5}$	1.1	0.94	0.74	0.65	0.57
Flexometer[b]					
Permanent set, %	28	26	22	21	11
Dynamic drift, %	23	19	17	15	7
Temperature rise, ° F	102	88	93	73	66
Appearance	Porous	Slightly Porous	Slightly Porous	Dense	Dense

[a] Formulation: Butyl 218—100, MPC—50, Process oil—15, Stearic acid—1.0, Zinc oxide—5, Tellurium diethyldithiocarbamate—1.0, Benzothiazolyl disulfide—1.0, Sulfur—1.25, "Elastopar"—as indicated. Compounds vulcanized 40′ @ 307° F.
[b] Test: Initial temperature 212° F, 0.25″ stroke, 89#/in^2 load, 32 cps.

promoting heat treatment effects as noted in the flexing behavior shown in Table XVII. Some idea of the evolution of promoting agents and their profound effects on the development of a butyl tire durable under extreme conditions of overload and high speed are shown in the indoor wheel records in Tables XVIII and XIX. The indications of these indoor wheel tests have since been amply confirmed by road tests and mass consumer evaluation. Whereas originally the durability was low, very likely due to high internal viscosity of the vulcanizates, now it is more than acceptable. This evolution of a high safety margin in butyl tires is certainly attributable to the development of heat treatment processes beginning with the early work of Gessler and his inquiry into the nature of polymer-pigment habit.

This work led to considerable interest in the role of surface activity of blacks in the heat treatment process and reinforcement in general. Zapp and Gessler[76] made a study of the reinforcement of butyl with carbon black and the

TABLE XVIII

CHEMICAL PROMOTION AND TIRE DURABILITY—CLEATED WHEEL[a] (BUCKLEY[75])

Feature	Load	T° F[b]	Failure miles	Failure
SBR hevea control	135	230	4650	Separation
Butyl—no promoter	125	230	2150	Reversion
Butylac-33 (carcass only)	135	230	4000	Separation
Butylac-33 (carcass and tread base)	155	215	6500	Separation—cap and base
Elastopar (carcass only)	145	210	5400	Separation
Elastopar (carcass, tread base and cap)	155	220	6400	Separation

[a] Wheel diameter: 67.5″
Cleats 6—2″ × ¾″ at 90°, 45° and 135° (repeated)
Speed: 45 mph
Inflation pressure: 24 psi initial
Load:

Miles	Load, % of tire and rim association specifications
0–4000	125
4000–5000	135
5000–6000	145
6000–7000	155
7000–Failure	165

[b] Running tire temperature at equilibrium, measured by contained air technique.

TABLE XIX

CHEMICAL PROMOTION AND TIRE DURABILITY.
HIGH-SPEED WHEEL[a] (BUCKLEY[75])

Feature	T° F[b]	Max. MPH	Failure
SBR hevea control	220	95	Separation
Butyl—no promoter	240	85	Reversion
Butylac-33 (carcass only)	210	95	Separation
Butylac-33 (carcass and tread base)	226	95	Separation
Elastopar (carcass, tread base and cap)	223	105	Separation

[a] Wheel diameter: 10 feet
Load: 100% TRA
Inflation pressure: 24 psi initial
Speed: 75 mph initial with step-up 5 mph each hour until failure
[b] Running tire temperature at maximum mph indicated.
Temperature measured by contained air technique.

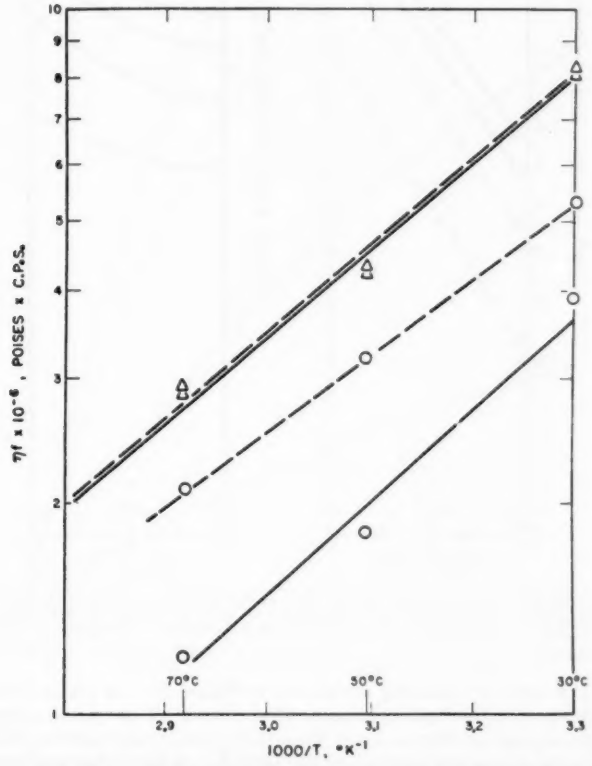


FIG. 62.—Effect of surface pH of channel black on the damping properties of untreated and heat-treated butyl systems. Dashed lines refer to devolatilized EPC black, pH-9.2, and solid lines to standard EPC black, pH—4.9. Triangles refer to untreated, and the circles to heat-treated mixes (Zapp and Gessler[75]).

specific action of surface oxygen. One of their experiments consisted of removing surface oxygen from EPC channel black by devolatilization in an electric muffle furnace at 1600° F for 3 hours. The black was allowed to cool under vacuum to minimize regain of oxygen. Their comparative results for standard EPC and devolatilized EPC in the heat treatment process and the effect on

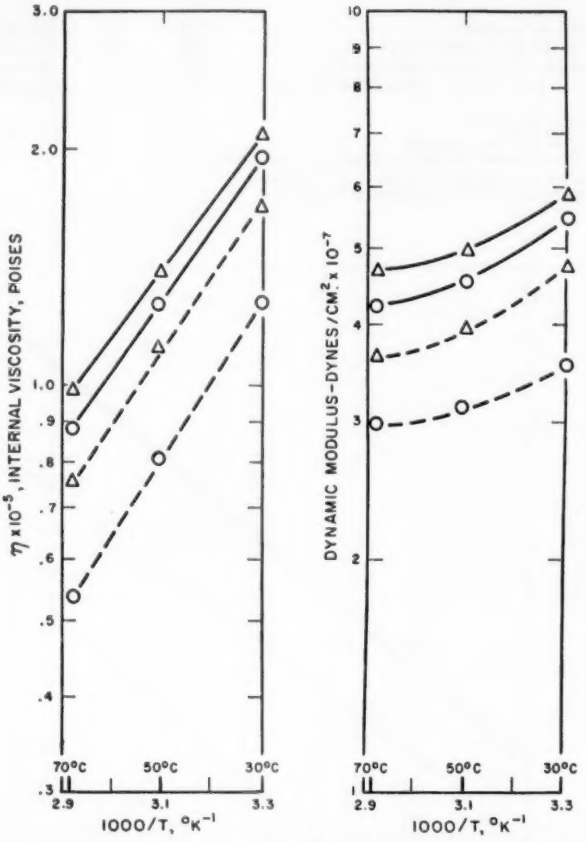


FIG. 63.—Effect of surface oxidation of HAF black on the damping properties of untreated and heat-treated butyl systems. Dashed lines refer to oxidized HAF black, pH-4.7 and the solid lines to standard HAF black, pH-8.7. The triangles refer to untreated, and the circles to heat-treated mixes (Zapp and Gessler[76]).

reduction of absolute damping are shown in Figure 62. A major dependence of the efficiency of the heat treatment effect on surface oxygen is noted. Reversing the procedure, these authors then oxidized a furnace carbon (HAF) in a stream of oxygen at a temperature of 250–300° F. A black was produced which contained 3.82 per cent oxygen according to the Unterzaucher method. Thus, a furnace black was converted to about the same oxygen content as a commercial

channel black (3.17 per cent). The comparison of the channel black and the oxidized HAF black is made convenient by the fact that they are in the same particle size range, 28 to 32 millimicrons. The effect of the oxidation of HAF black in its activity in the heat treatment process as reflected in reduced absolute damping is shown in Figure 63. The same effect was noted in the extension of

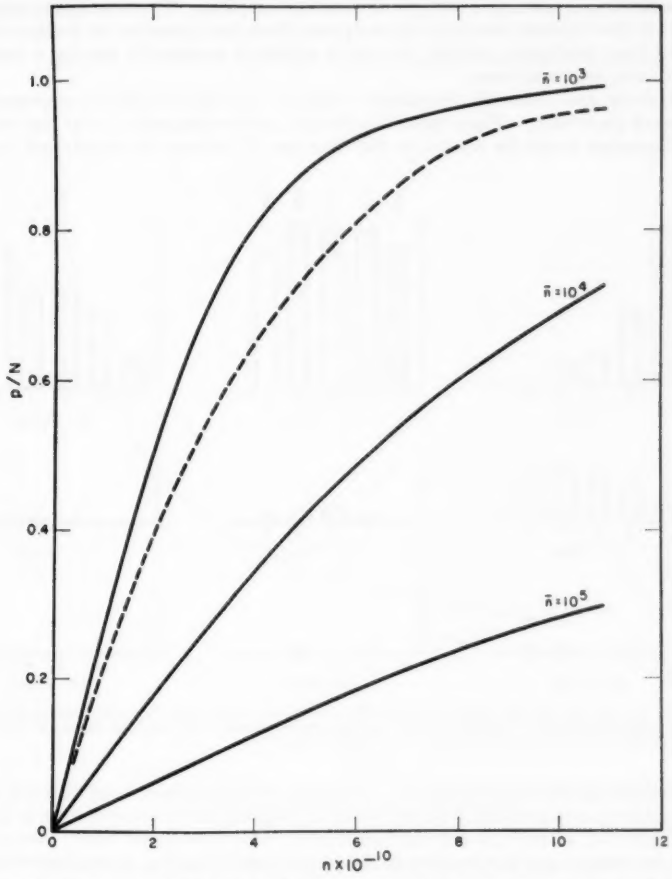


FIG. 64.—Theoretical dependence of dispersion on a number of carbon black-polymer bonds for aggregates of various sizes (Rehner and Gessler[78]).

this work to an SRF black. A further advantage from an oxy-surface furnace black was observed by these authors in an improvement of the desired "plateau" effect in ultimate properties with continued vulcanization. Normally the furnace blacks in butyl reach a rather sharp maximum in the tensile strength-time of vulcanization curve and tensile strength falls off rapidly there-

after. With the oxy-surface furnace carbons, this phenomenon was much less pronounced.

These authors make reference to the distinct difference in the relation of state of surface oxidation of furnace carbons to the properties obtained in a high diene polymer such as SBR and a low diene polymer such as butyl. It has been reported[77] that oxidation of a furnace carbon provided no advantage over the normal furnace carbon in the reinforcement of SBR. These authors suggest that, if the ethylenic bonds in the polymer chain are operative as reactive sites in the heat treatment process, low diene polymers necessarily require a carbon with more active surface.

Rehner and Gessler[78] developed a theory of heat treatment expressed in terms of dispersion. They based this theory on the assumption that the degree of dispersion would be related to the number of carbon black-polymer bonds

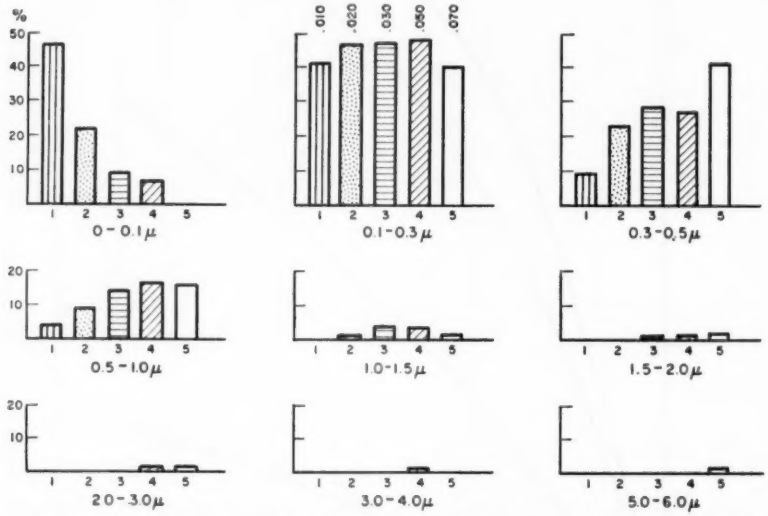


FIG. 65.—Agglomerate size distribution of butyl-carbon black dispersion. Data are based on a statistical analysis of electron micrographs. Insert numbers at top of bars in top-center of figure represent mill setting in inches for dispersion experiments (Ford and Mottlau[79]).

formed during the heat treament. The theoretical dependence of dispersion on a number of carbon black-polymer bonds for aggregates of various sizes is given in Figure 64. Here n is the number of carbon black-polymer bonds formed by heat treatment, p is the fraction of the carbon black that has been dispersed into discrete particles, N is the total number of ultimate particles present at a given time, and $\bar{n}$ is an assumed aggregate size. Thus, the ratio p/N is the fractional degree of dispersion. If proper correction is made for the disappearance of reactive sites (chemical unsaturation) during the process the upper curve can be replaced with the dotted curve.

It is interesting to note that dispersion increases most rapidly in the early stages of bond formation and approaches the limiting value of unity asymptotically. The shape of these dispersion-carbon black-polymer bond curves should

be compared with the effects of continued heat treatment on electrical resistivity.

Ford and Mottlau[79] showed that the dispersion of carbon black in a butyl polymer under different milling conditions could be well characterized by several different types of methods. Using electron micrograph techniques in a manner similar to Ardenne and Beischer[80] and Hall and associates[81] they were able to construct aggregate size distribution charts as typified in Figure 65. They used

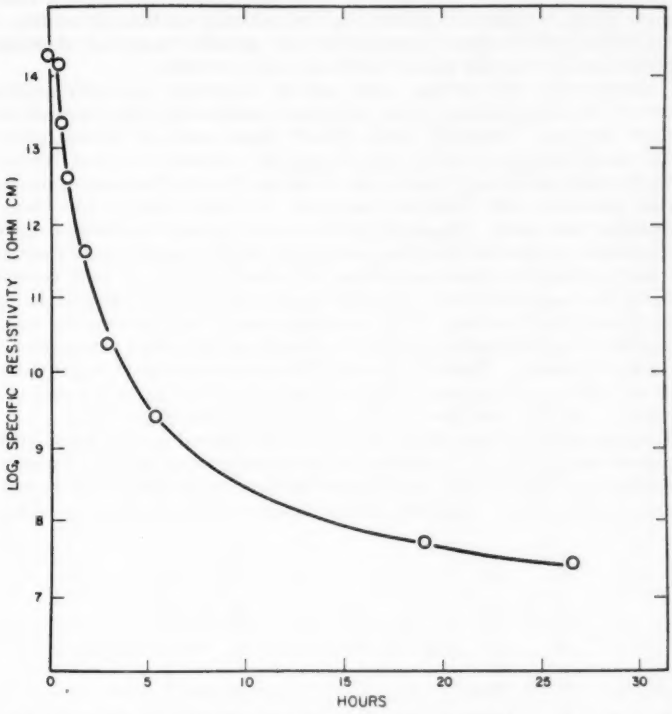


FIG. 66.—Drift in resistivity of an unvulcanized SRF-butyl system under constant electrical potential at room temperature (Ford and Gessler[82]).

these distribution data as a reference and found very good agreement in values for gross, medium and fine dispersions in sedimentation and rheological tests.

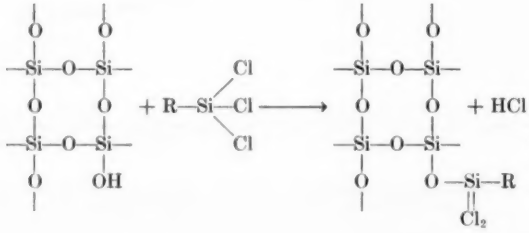
Some of the complexity of experiments in the field of study of dispersions in carbon black-polymer systems is recognizable from the work of Ford and Gessler[82]. They observed that when an unvulcanized composition of SRF-butyl polymer was maintained under constant electrical potential at room temperature, a decided drift downward in electrical resistivity took place. A typical experiment of this type is recorded in Figure 66. These authors concluded that some form of particle alignment was induced by the current.

However, the effect of the drift on viscoelastic properties was minor. Thus, they concluded that the reaggregation involved relatively weak forces.

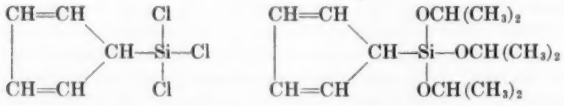
Mineral pigments and heat treatment relative to dynamic behavior.—Gessler and Rehner[83] found that inorganic pigments such as hydrated silica could be made to respond to the heat treatment process. It was found necessary to use a promoting agent to achieve this effect. The benzoate ester of *p*-quinone dioxime was found to have sufficient promoting activity. These authors theorized that the quinone dioxime compound reacted with the hydroxyls on the silica particle surface and through such associations and reaction with the polymer chains resulted in destroying the cohesive particle structure. The vulcanizates derived were characterized by greatly improved stress-strain properties and by sharply reduced stiffness and hysteresis.

Unfortunately, this system could not be considered generally applicable because of the discoloration of the vulcanizate associated with reactions of the quinone dioxime. Together with Wiese[84] these authors investigated the surface modification of silica and subsequent response to heat treatment. Hydrated silica as a slurry in a hexane solution of organohalosilanes reacted to provide pigments with modified surfaces. Cyclopentadienyl and vinyl trichlorosilane were used. Desirable effects were obtained in extension modulus and reduction of absolute damping with both modified products. They noted that sharp changes in these properties are obtained without heat treatment. However, the heat treatment was found to add to the general value of the effects of the surface modification. These authors showed that the reaction could be accomplished by adding the silane to the butylhydrated silica composition on a mill or in a Banbury. The evolution of HCl during this type of experiment was taken as evidence of reaction. The reaction is believed to be a result of condensation involving both free and bound water on the pigment.

The importance of the silane structure was pointed out by these authors. It has been suggested that halosilanes react at the particle surface through unimolecular condensation with the hydroxyl groups of the silica held on the pigment as bound water. Hydrated silica modified with a silane in which the



chlorine atoms were replaced by isopropoxy groups did not provide pigments responsive to heat treatment. This work gives ample evidence that one of the



Responsive *Nonresponsive*

routes to increasing the usefulness of pigments and controlling their effect on dynamic behavior of polymer systems would be through further research on their surface chemistry.

VIII. DEGRADATION

The attainment of elastomeric behavior through the medium of sufficiently long and mobile chains linked together into a permanent network is of reduced value if degradation of such a structure takes place readily. It is instructive to consider degradation by pyrolysis in vacuum, in photolytic processes, in an atmosphere of oxygen or ozone, and under the influence of high energy sources. Pyrolysis in vacuum would appear to be an important base line since it would

TABLE XX

PYROLYTIC FRACTIONATION OF POLYISOBUTYLENE (VISTANEX) (MADORSKY ET AL.[86])

Experiment number	Weight of samples, mg	Temp., °C	Duration, min	Fractions in weight per cent of original sample: I Residue	II Nonvolatile at room temperature	III Volatile at room temperature	IV Gaseous fraction	Fraction III in percentage of total pyrolyzed part
1	24.9	313	30	97.2	2.4	0.4	0	14.2
2	22.5	344	30	98.0	11.3	5.7	Trace	33.5
3	56.7	361	30	64.3	26.3	10.3	0.07	28.9
4	58.0	362	30	65.2	24.3	10.4	0.08	29.9
5	45.4	378	30	20.7	52.4	26.8	0.12	33.8
6	52.7	401	30	0.2	68.5	31.1	0.20	31.2
7	82.9	401	30	0.3	79.3	20.2	0.22	20.3
8	49.2	401	30	0.1	69.4	30.3	0.19	30.3
9	49.6	402	30	0.4	68.4	31.0	0.22	31.1
10	48.9	402	30	0.5	70.8	28.5	0.23	28.6
11	23.2	407	30	0.4	66.6	32.8	0.22	32.9
12	55.2	415	30	0.3	68.9	30.5	0.25	30.6
13	60.0	418	30	0.1	69.0	30.7	0.22	30.7
14	20.9	450	30	0.2	64.7	34.9	0.22	34.9
15	45.4	460	30	0.0	67.0	32.8	0.22	32.8

Average fraction III in percentage of total pyrolyzed part for all experiments except 1 and 7 ..... 31.5 ± 0.8

depend largely on the bond strengths in the material under study. Photolysis is of both practical and fundamental importance because of the frequent use of elastomers in the presence of degrading wavelengths and also because of the need for understanding the manner in which this form of energy is transferred into a degrading source. Oxidation and the resulting loss of elastomeric properties and the surface cracking due to ozone attack are of obvious importance. The more recent work on changes in polymers under high energy conditions represents a new approach to an understanding of excited molecules.

It is recognized that degradation of polymer networks can take place under the influence of mechanical forces. Sample failure in ultimate tensile, fatigue, abrasion and tearing processes are evidence of this fact. However, this aspect of the problem of degradation will not be considered here. Some attention has already been given to this area of polymer behavior in other sections of this review.

TABLE XXI

MASS SPECTROMETER ANALYSIS OF FRACTION IIIA OBTAINED IN THE PYROLYSIS OF POLYISOBUTYLENE (MADORSKY ET AL.[16])

Experiment number		3	4	7	9	10	12	13	Average for all Experiments	Average component in percentage of total pyrolyzed part, wt. %
Temperature of pyrolysis, ° C		361	362	401	402	402	415	420		
Part pyrolyzed, per cent		35.7	34.8	99.7	99.6	99.5	99.6	99.9		
Component	Molecular weight	mole per cent								
Isobutene	56.1	90.3	89.6	93.9	92.7	93.0	93.0	92.8	92.8	20.180
Isobutane	58.1	1.4	1.3	1.9	1.5	1.6	1.6	1.7	1.6	0.320
Pentenes	70.1	0.5	0.7	—	0.4	—	—	0.2	0.2	0.048
Neopentane	72.1	7.8	8.4	4.2	5.4	5.4	5.4	5.3	6.0	1.502
Total	—	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	22.050
CO_2	44	Trace	Trace	Trace	Trace	Trace	Trace	Trace	—	—

Pyrolysis in high vacuum.—Wall[85] and Madorsky and associates[86] at the National Bureau of Standards studied the pyrolysis of polyisobutylene in high vacuum at high temperatures. In the experiments of Madorsky, a sample of commercial polymer was first purified by dissolving in benzene and precipitating with methanol. The purification was repeated twice. A layer of polymer 17–50μ thick was laid down from solution and used in the pyrolysis experiments. The duration of pyrolysis was maintained at 30 minutes throughout all experiments over a high temperature range. The products of pyrolysis were defined as: (I) nonvolatilized fraction remaining as residue after pyrolysis, (II) a fraction volatile at the temperature of pyrolysis but nonvolatile at room temperature, (III) a fraction volatile at room temperature and (IV) a gaseous fraction. The results of this type of pyrolytic fractionation of polyisobutylene for several temperature ranges are shown in Table XX. It may be seen that pyrolysis begins at 300° C and becomes extremely rapid at 400° C and above, going almost to completion.

The fraction (III) representing the pyrolytic products volatile at room temperature was analyzed by Madorsky in the mass spectrometer to provide the data shown in Table XXI. The most significant portion of this fraction

TABLE XXII

AMOUNT OF MONOMER–TYPE MOLECULES IN THE VOLATILE PRODUCTS OF THERMAL DEGRADATION OF POLYMERS (MADORSKY[87])

Polymer	Weight per cent of total pyrolyzed part	Mole per cent of total pyrolysed part
Polymethylmethacrylate	100	100
Poly-α-methylstyrene	100	100
Polyisobutene	32	78
Polystyrene	42	65
Polybutadiene	14	57
SBR	12	52
Polyisoprene	11	44
Polyethylene	3	21

was found to be isobutene averaging 92.8 per cent over all experiments. Neopentane content averaged 6.0 per cent with a small amount of isobutane and pentenes present.

Fraction (II) representing pyrolytic products volatile at the temperature of pyrolysis but not at room temperature was characterized by molecular weight measurements. The average molecular weight of these fractions resulting from pyrolysis at a number of temperatures was 543 which represents a chain fragment containing between 9 and 10 monomer units.

Fraction (IV) was found to contain methane and small amounts of carbon dioxide, hydrogen, oxygen and carbon dioxide.

From an analysis of the production of monomer or monomer type products during pyrolysis, some conclusion may be made as the nature of the chain breaking process. Madorsky[87] summarized such information for a number of polymers. This summary is shown in Table XXII. It is reasoned that the production of a large amount of monomer type products during pyrolysis indicates a terminal initiation of chain breakage followed by a progressive zip reaction along the chain. Conversely, pyrolytic production of large molecules indicates a more random chain breakage. On this basis, polymethylmethacrylate would appear to pyrolyze by a preferred terminal breakage process while

polyethylene would follow a random course. Polyisobutylene would be intermediate showing chain breakage by both the terminal-zip process and the random process.

The relative thermal stability of vinyl and diene polymers was examined by Madorsky and the results are plotted in Figure 67. It is shown that polyisobutylene is intermediate in this family of polymers relative to the temperature and extent of pyrolysis. Madorsky points out that the carbon-carbon bonds in a polymer chain can be weakened, with respect to thermal stability, by the presence of secondary or tertiary carbons.

Despite the high temperatures usually used in pyrolytic experiments, they are useful as guides to other forms of degradation under milder conditions. Thus, the study of the purely thermal stability of a polymer may indicate the weakest point in degradation processes under photochemical, oxidative and high energy conditions.

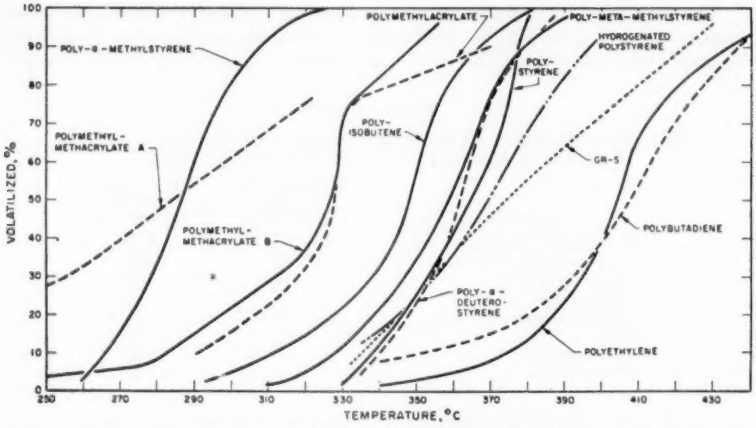


FIG. 67.—Relative thermal stability of vinyl and diene polymers (Madorsky[86]).

Photochemical degradation.—Bateman[88] in a study of the photochemical breakdown of unvulcanized natural rubber in vacuum at room temperature showed a definite dependence on wavelength. Using a mercury lamp source, it was found that 3650 A was the longest effective wavelength in this spectrum. The range 2350–2850 A was the most efficient in terms of rate of polymer breakdown for a given light intensity. A very sharp decrease in the efficiency was noted above 2800 A. Bateman considered that the absorption of quanta at 2800 and 3600 A raises the molecular energy by 100 and 78 kcal per g-mol., respectively. Thus, the dissociation energies of normal C—H and C—C bonds would be approximated. In addition, in a natural rubber chain, bonds of lower dissociation energy are present. According to Bateman, allylic resonance would reduce the dissociation energy of α-methylenic C—H bonds to about 80 and that of the central C—C bonds to about 43 kcal per g-mol. Thus, the susceptibility of the chain to degradation under photochemical conditions would appear very probable on purely energy considerations. Because of the sharp break in efficiency at 2850 A, Bateman reasoned that in the initial photochemical scission reaction breakage of C—H bonds should predominate over C—C bonds.

However, the complexity of the decomposition does not allow a clear definition of the primary dissociation act.

Eby[59] studied the photochemical breakdown of pure gum vulcanizates of butyl exposed to light of various wavelengths in vacuum and in air. No appreciable breakdown of the vulcanizate was observed at any wavelength in vacuum. Breakdown in air occurred but only when the wavelength was less than 4600 A. Eby observed further that the more injurious wavelengths are between 3000–4000 A with strong indications that the maximum wavelength for extensive breakdown is about 3600 A. It is of interest to note the similarity of the observations on butyl relative to wavelength effects and those made by Bateman on natural rubber. Also, it may be noted that there is a great similarity for the wavelength effects on the photochemical degradation of all hydro-

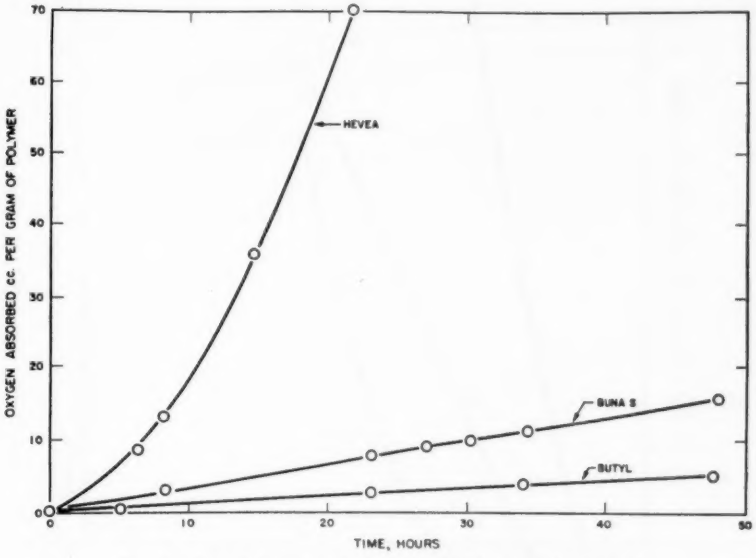


FIG. 68.—Rate of absorption of oxygen at 130° C by gum vulcanizates of butyl and other elastomers (Mesrobian and Tobolsky[59]).

carbons. Eby examined a large number of antioxidants as protective agents against surface deterioration of butyl vulcanizates under photochemical conditions. He found certain aryl amines effective but they were unsatisfactory because of very intense coloration. Formation of a peroxide or a free radical through the methyl groups has been suggested as a possible mode for the degradation. Stabilization research therefore would have to provide agents which could react with the peroxide or free radicals to produce inactive compounds. Carbon blacks in butyl vulcanizates are suspected of having this facility. However, no such stabilization is yet available for pure gum compounds or those containing non-black fillers.

Oxidative degradation.—The importance of olefin chemistry in the oxidative degradation of polymers and crosslinked networks is now well known. The relative oxygen absorption of pure gum vulcanizates of natural rubber, Buna-S

and butyl as reported by Mesrobian and Tobolsky[90] in Figure 68 is typical. Although low functionality, in terms of number of double bonds in the chain would appear to be very important, the nature of the chain also is of importance. Mesrobian and Tobolsky compared the oxygen absorption of natural rubber,

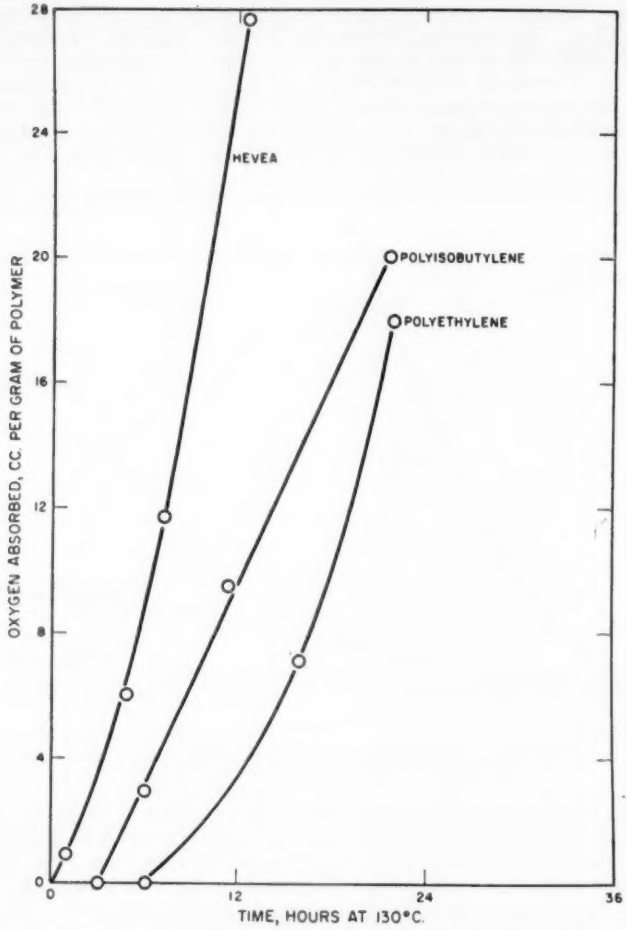


FIG. 69.—Rate of oxygen absorption by polymers of various chain structure (Mesrobian and Tobolsky,[90]).

polyisobutylene and polyethylene. Their rate curves for these three polymers are shown in Figure 69. In the order previously given, these polymers represent (1) a polymer chain containing high concentrations of both double bonds and methyl side groups, (2) a polymer chain containing no double bonds but a very

high concentration of methyl side groups and (3) a polymer chain containing neither double bonds nor side groups. Thus, the combination of unsaturation and side groups, as expected, leads to a high rate of oxygen absorption and the resulting effects in oxidative degradation. It should be noted that the methyl side groups are an important aspect of degradation for "saturated" molecules such as polyisobutylene. The inferences made here relative to polyisobutylene are transferable to butyl with its low unsaturation.

This reviewer would like to confine the portion of this review dealing with oxidative degradation to the growing realization that there is a relationship

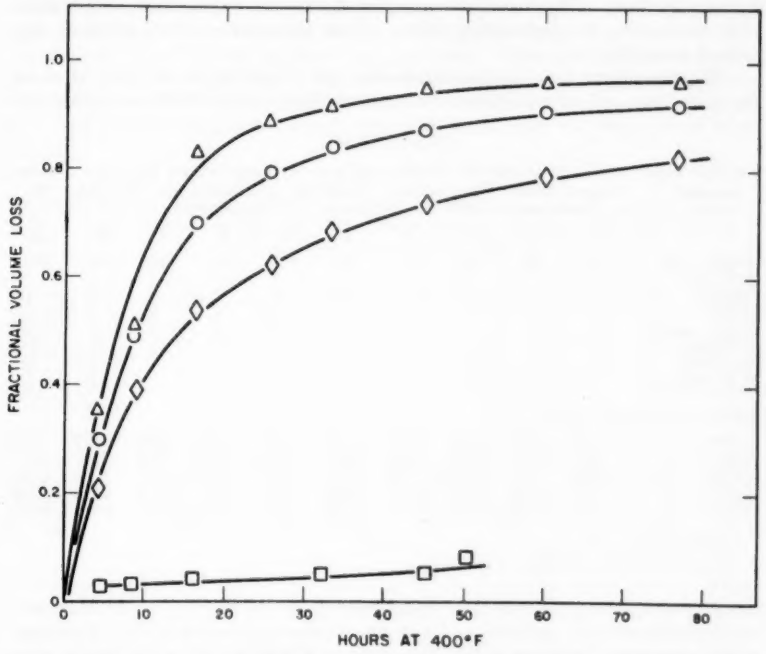


FIG. 70.—Fractional volume loss of Vistanex L-80 (▲), Enjay Butyl 268 (●), MD-551 (◆), and MD 551 vulcanized thiazolyl-thiuram-zinc oxide system (■) when exposed in air at 400° F. The first three polymers contain no vulcanizing materials (Buckley and Clayton[91]).

between oxidation and vulcanization. Buckley and Clayton[91] studied the high temperature degradation of vulcanizates of MD-551 chlorine containing copolymer of isobutylene-isoprene. As a preliminary to these experiments, they found that the unvulcanized polymers Vistanex (polyisobutylene), Enjay Butyl 218 and MD-551 degraded in a simple volatility test with about equal readiness. Their data are shown in Figure 70 along with data for the volatility loss of a vulcanizate of MD-551. The presence of unsaturated bonds in Enjay Butyl 218 polymer and unsaturated bonds plus chlorine in the MD-551 chains would seem to show little effect on the rate of volatilization of these polymers. The effects of polymer composition are somewhat obscure in this comparison

since commercial polymers containing different amounts of antioxidant were used. The MD-551 polymer contained the highest concentration of antioxidant and the Vistanex L-80 the lowest. However, the effect of vulcanization on the resistance of this polymer to degrade to small volatile fragments is quite marked and unmistakable. The production of a three-demensional network could in itself limit the extent to which volatile molecules are generated. However, it should be noted that the carbon-carbon bonds of the polyisobutylene portion of the networks are still free to degrade as readily as observed in the case of Vistanex L-80. This is particularly true when it is considered how the numbers of these bonds predominate over those specifically formed in the crosslinking reaction. These authors postulated that an explanation, other than that embodying the restraining effects of the three-dimensional network, appeared necessary.

They suggested that the materials used for vulcanization or possibly those resulting from vulcanization could be contributing to the oxidative stability of

TABLE XXIII

VOLUME FRACTION LOSS AT 400° F OF VISTANEX L-80 CONTAINING VARIOUS COMBINATIONS OF COMPOUNDING MATERIALS. SAMPLES PREPARED BY MOLDING 35 MINUTES AT 307° F (BUCKLEY AND CLAYTON[91])

	1	2	3	4	5	6	7	8	9	10
Vistanex L-80[a]	100	100	100	100	100	100	100	100	100	100
Stearic acid	—	1	1	1	1	1	1	1	1	1
Zinc oxide	—	—	3	3	3	3	3	3	3	3
TMTDS	—	—	—	1	1	1	1	1	1	1
BTDS	—	—	—	—	2	2	2	2	2	2
Lt. calc. magnesia	—	—	—	—	—	2	2	2	2	2
HAF black	—	—	—	—	—	—	50	50	50	50
Zinc chloride	—	—	—	—	—	—	—	2	2	2
Succonox 12[b]	—	—	—	—	—	—	—	—	2	2
Amberol ST-137[c]	—	—	—	—	—	—	—	—	—	5
Volume Fraction Loss at 400° F										
4 hours	.120	0.128	0.124	0.013	0.016	0.015	0.017	0.012	0.014	0.019
8 hours	0.252	0.226	0.234	0.105	0.017	0.018	0.019	0.014	0.015	0.020
16 hours	0.487	0.462	0.493	0.342	0.019	0.020	0.019	0.015	0.017	0.021
32 hours	0.737	0.631	0.742	0.587	0.066	0.140	0.021	0.018	0.020	0.023
48 hours	0.824	0.789	0.824	0.678	0.108	0.213	0.029	0.019	0.023	0.027
68 hours	0.842	0.838	0.913	0.677	0.185	0.344	0.030	0.021	0.026	0.030

[a] Enjay Company Inc.
[b] Sumner Chemical Company.
[c] Resinous Products and Chemical Company.

the polymer chains. Thus they could reduce the number of chain fractures leading ultimately to molecules of a chain length volatile at 400° F. This suggestion contains the concept that the material showing such stabilizing action could function either to prevent chain fracture or assist in recombinations of degraded molecules.

The ability of certain compounding ingredients to act as stabilizers was tested by addition to Vistanex L-80. Initially, at least, this polymer may be considered as incapable of forming a crosslinked network. Thus if stabilization occurs it should be traceable to some cause other than the production of a network and its accompanying restraint on generation of small volatile molecules. The materials were added as combinations to Vistanex L-80 as shown in Table XXIII. Small samples were then exposed to air at 400° F and weighed periodically. The combination of stearic acid-thiuram-zinc oxide showed stabilizing power at early times. This faculty was greatly enhanced by the further addition of benzothiazolyl disulfide. Carbon black (HAF) exhibited tremendous retardant power and this unfortunately obscured the action of the remaining

combinations including zinc chloride, an antioxidant, and a methylol resin normally used as a crosslinking agent.

The effect of each material added singly to Vistanex L-80 is shown in Table XXIV. A cross comparison of the data in these two tables leads to some inferences which may be of value in a further understanding of vulcanizate stability at high temperatures. Zinc oxide and thiuram by themselves show no effect. Thus the trend towards improvement noted previously must be due to a combination of zinc oxide and thiuram. Benzothiazolyl disulfide by itself is effective but considerably less so than in the combination with zinc oxide-thiuram-stearic acid. Carbon black addition again shows high capacity for restricting volatile loss and the loss is even lower than when the carbon black is used in combinations. The observation on the effectiveness of zinc chloride in retarding degradation to small molecules is important. This salt is formed during the vulcanization of MD-551 compositions containing zinc oxide. The corresponding zinc halide is very likely formed during the vulcanization of all polymers containing active halogen and zinc oxide, and the presence of such

TABLE XXIV

VOLUME FRACTION LOSS AT 400° F ON VISTANEX L-80 CONTAINING VARIOUS COMPOUND MATERIALS ADDED SINGLY. SAMPLES PREPARED BY MOLDING 35 MINUTES AT 307° F (BUCKLEY AND CLAYTON[91])

	1	2	3	4	5	6	7	8
Vistanex L-80	100	100	100	100	100	100	100	100
Zinc oxide	3	—	—	—	—	—	—	—
TMTDS	—	1	—	—	—	—	—	—
BTDS	—	—	2	—	—	—	—	—
Lt. calc. magnesia	—	—	—	2	—	—	—	—
HAF black	—	—	—	—	50	—	—	—
Zinc chloride	—	—	—	—	—	2	—	—
Succonox 12	—	—	—	—	—	—	2	—
Amberol ST-137	—	—	—	—	—	—	—	5
Volume Fraction Loss at 400° F								
4 hours	0.120	0.086	0.009	0.117	0.007	0.016	0.009	0.010
8 hours	0.220	0.191	0.056	0.168	0.007	0.023	0.009	0.009
16 hours	0.515	0.561	0.215	0.415	0.007	0.090	0.070	0.115
32 hours	0.758	0.796	0.402	0.636	0.007	0.177	0.559	0.652
48 hours	0.833	0.848	0.511	0.766	0.007	0.231	0.764	0.824
68 hours	0.845	0.848	0.717	0.786	0.009	0.264	0.837	0.884

materials could exert appreciable effect on the high temperature stability of the vulcanizates. Succonox 12 (an antioxidant, N-lauroyl-*p*-aminophenol) shows normal effectiveness but appears to be quickly expended. It was anticipated that Amberol ST-137 (a methylol phenol resin discussed previously in this review) would exhibit stabilizing power because of its phenolic structure. Taking the resin at an average molecular weight of 800, it would appear to be, on an approximate equimolar basis, as effective as the N-lauroyl-*p*-aminophenol in retarding degradation under these conditions.

It would thus appear that the materials remaining in the vulcanizate after the vulcanization could be important in determining oxidative stability. Stabilization research could very likely profit from a consideration of the materials chosen for an elastomeric composition with an eye to their potential dual role in vulcanization and stabilization.

Confirmation of this concept is found in the work of Fletcher and Fogg[92] on the heat aging of natural rubber vulcanized with tetramethylthiuram disulfide. The heat aging resistance of natural rubber vulcanizates obtained with tetramethylthiuram disulfide in the absence of sulfur is well known. These authors

deduced from the combined results of Scheele and coworkers[93] and Dunn and Scanlon[94] that the product of the reaction of this accelerator and zinc oxide, zinc dimethyldithiocarbamate formed in situ during vulcanization, may be partly responsible for the proven heat resistance of the vulcanizate. Scheele and coworkers showed that two-thirds of the thiuram during vulcanization in the presence of zinc oxide was converted to the zinc thiocarbamate. Dunn and Scanlon showed that a wide range of thiocarbamates, including the zinc salts, suppressed degradation of an acetone extracted vulcanizate resulting from crosslinking with the thiuram. The beneficial effects were not noted when sulfur was present in the original vulcanizate. Fletcher and Fogg showed that removal of the thiocarbamate by extraction substantially reduced the age resist-

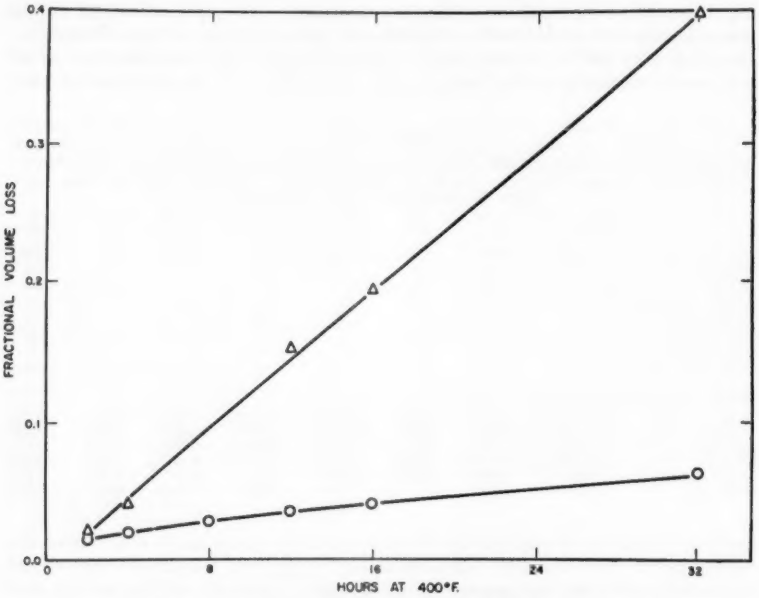


FIG. 71.—Fractional volume loss of an MD-551 vulcanizate extracted (Δ) and unextracted (○) (Buckley and Clayton[81]).

ance of the original unextracted vulcanizate. They were able to reclaim a substantial part of the age resistance by adding the thiocarbamate back into the crosslinked network by a process of allowing the vulcanizate to swell in a solution of appropriate concentration of zinc dimethyldithiocarbamate.

Craig[60], in reviewing the work of Lorenz, Scheele and Redetzky, pointed out the readiness of formation of zinc diethyldithiocarbamate from the reaction of zinc oxide and the corresponding thiuram. It is of importance that an appreciable concentration of this salt would be available during most of the vulcanization process. Thus, it would appear that a concentration sufficiently high to avoid chain degradation during high temperature exposure would be present.

General support for these concepts is supplied by the work of Buckley and

Clayton who found that the removal of reaction products from a vulcanizate of MD-551 profoundly affected the resistance to degradation. Their data are shown in Figure 71. The vulcanizate used in this experiment contained: polymer 100, zinc oxide 3, stearic acid 1, tetramethylthiuram disulfide 1, and benzothiazolyl disulfide 2. The extraction procedure consisted in soaking the vulcanizate in a 50–50 volume mixture of oleic acid and benzene for 5 days at room temperature followed by Soxhlet extraction with methyl ethyl ketone. This procedure is known to remove substantially all of the materials in the polymer with the exception of zinc sulfide. Of particular importance is the

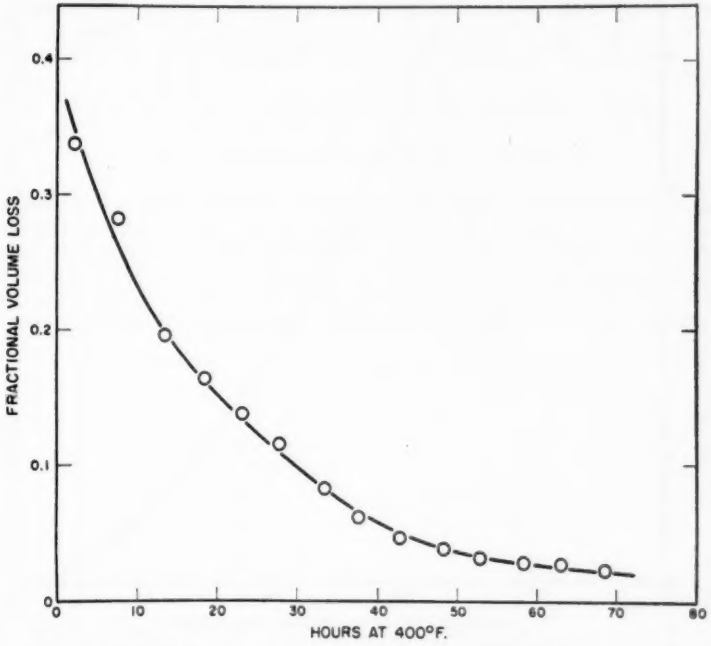


FIG. 72.—Fractional volume loss rate based on the incremental changes in volume of samples for each successive 5-hour period of exposure at 400° F. Data taken from smooth curve of Vistanex L-80 shown in Figure 70 (Buckley and Clayton,[9]).

fact that two compounds, zinc dimethyldithiocarbamate and zinc chloride known to be formed in the vulcanization of this composition, are almost completely removed. Their very probable action as stabilizers for the unextracted polymer is apparent in these data.

It is of considerable interest that Dunn and Scanlon found that the thiocarbamates (except cobalt and iron salts) are powerful retarders of degradation (measured by stress relaxation) whether induced by heat or U.V. light. Thus, it would appear that some considerable promise exists for the problem of stabilizing against oxidative and photochemical degradations using the same type of protective agent.

The degradation studies of Buckley and Clayton allow some appraisal of the nature of the oxidative breakdown of polyisobutylene at advanced temperatures. Rate data, expressed in terms of volume fraction of polymer loss for a selected interval of heat exposure, are shown in Figure 72. The rate of breakdown is greatest in the early stages of exposure. Possibly, the highly oxidized fragments present in the latter stages of exposure can recombine and thus lessen the observed amount of polymer lost by volatilization. Rate data, expressed as the volume fraction loss relative to amount volatilized, are shown in Figure 73. The generation of small molecules would appear to be largely the

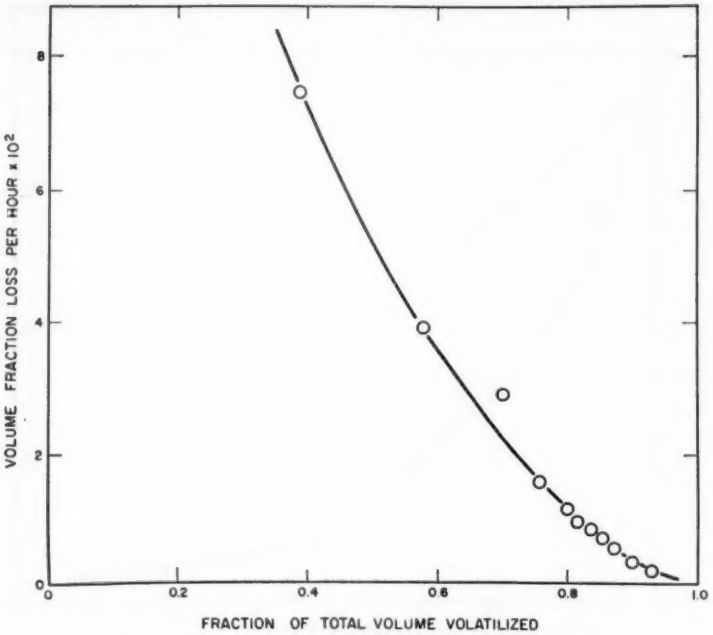


FIG. 73.—Rate of volume fraction loss relative to total volume fraction volatilized at 400° F (Buckley and Clayton,[91]).

result of a random process. Thus the mechanism of oxidative degradation would seem to bear some relation to Madorsky's observation of the pyrolytic breakdown of polyisobutylene in vacuum.

Ozone degradation.—One of the major areas of degradation of polymers is that related to ozone cracking. Despite the importance of this phenomenon, little attention has been given to attempts to define the controlling factors. It has been recognized that the tendency of a vulcanizate to produce cracks when stretched and exposed to an atmosphere of ozone is someway related to the presence of double bonds in the polymer chain. Butyl polymers therefore afford an excellent opportunity to study the phenomena of ozone attack and consequent mechanical effects. These polymers are available at chemical un-

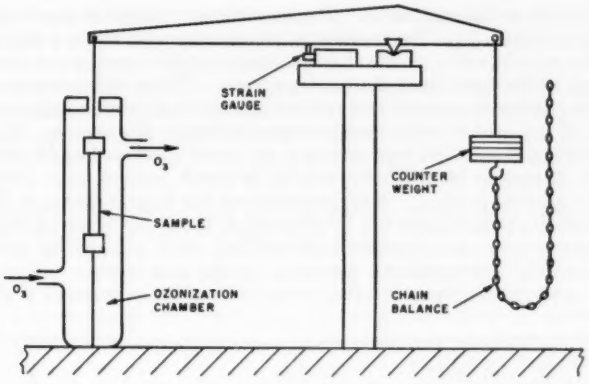


FIG. 74.—Ozonization apparatus (Buckley and Robinson,[95]).

saturation levels low enough to avoid the difficulties of a multiplicity of reaction points, such as is the case in high diene polymers. Moreover, the chemical unsaturation can be varied significantly without undue changes in the overall structure of the polymer. Buckley and Robison[95] took advantage of these features in a study of ozone attack on rubber vulcanizates. These authors followed the cracking of a specimen in substantial equilibrium when exposed in

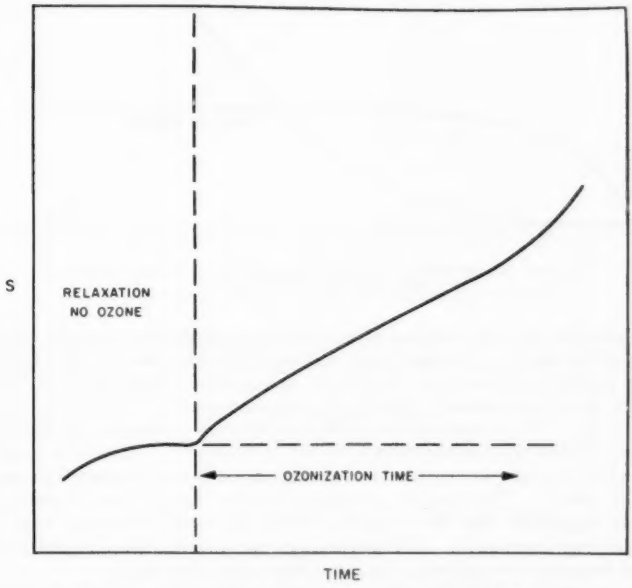


FIG. 75.—Typical relaxation and ozonization record (Buckley and Robinson,[95]).

a stream of air containing ozone. The apparatus employed is shown in simplified form in Figure 74. The cracking of the specimen produced a slight elongation of the sample and a resultant displacement of the beam and a corresponding change in the signal from the sensing system. These changes were recorded with time. After the sample had reached elastic equilibrium at some extension (usually 50 per cent or below) ozone was admitted to the sample. A complex curve showing three parts was obtained; an initial small and rapid change in S (increase in sample length), followed by a linear portion, and ultimately a higher accelerated portion. A typical curve of this type is shown in Figure 75. The complexity of this curve was interpreted as being due to the additive effects of two phenomena: the reaction and resulting chain scission on the original surface and the corresponding reactions on the new surface formed by the cracks. A schematic representation of this interpretation is shown in Figure 76.

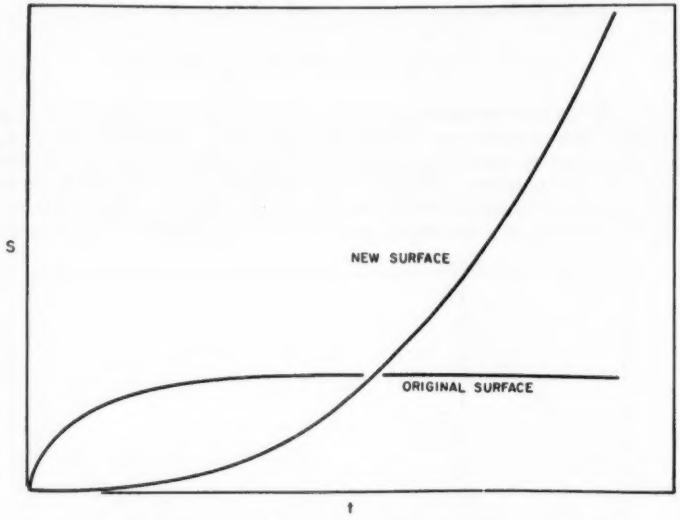


FIG. 76.—Representation of role of original and new surface in the cracking effect (Buckley and Robison[85]).

It was concluded that cracking rate calculations could be based on the linear portion of the curve. The initial small change in S was not of major significance for the purpose at hand and the highly accelerated change in S at extended exposure times represented a change in sample geometry beyond the objective of this work. The minor roles of ordinary physical relaxation mechanisms on change in S during an experiment is shown in Figure 77. Here it is found that the cracking leading to changes in S practically ceases when ozone is removed from the system. The rapidity of changes in this intermittent exposure study is highly suggestive that the reactions taking place are concerned only with a surface of very low depth. This particular observation was quite characteristic of most experiments performed in connection with this work.

The concept of the mechanism of ozone cracking here contains three parts: (1) chemical cleavage of the network chains at the double bonds must occur,

(2) energy must be stored in the chains to cause them to move apart upon cleavage making a void in the network structure, and (3) a multiplicity of such voids at the surface produces a visible crack.

The stored energy and the transformation of energy involved in the work of crack formation is obtained as follows: The equilibrium stress-length relation of a sample just prior to ozone exposure is given by:

$$Z_1 = kNTA\ (L - 1/L^2) \tag{1}$$

where A is the cross-section area and the other notations have their usual significance. The stored elastic energy is given by

$$W = kNTA\ (L^3 - 3L + 2)/2L \tag{2}$$

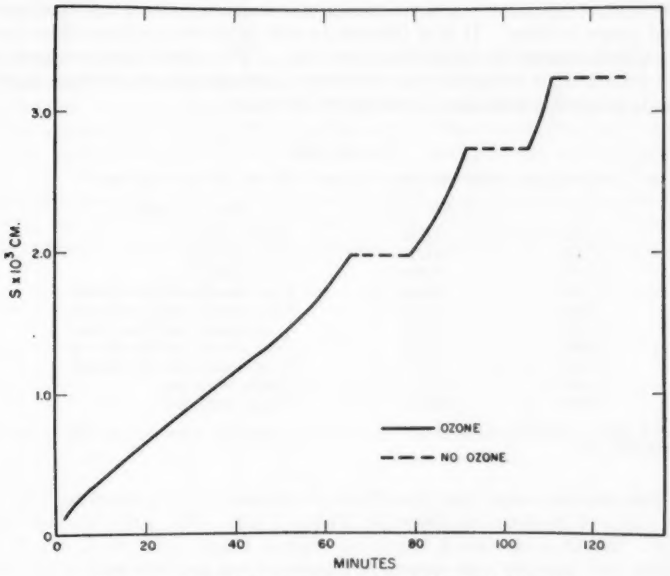


FIG. 77.—Intermittent exposure to ozone (Buckley and Robison[55]).

The force-length relationship of the movement of the beam yields a proportionality constant k'. Thus, the change in work in the sample due to cracking is

$$\Delta W = \int k'SdS = k'S^2/2 \tag{3}$$

The ratio of work change to the original work equals:

$$\Delta W/W = k'S/[2kNTA\ (L^3 - 3L + 2)/2L]$$

$$N = Z/kT\ (L - 1/L^2)$$

$$\Delta W/W = (k'S^2/2)1/Z_1 \frac{(L - 1/L^2)}{(L^3 - 3L + 2)/2L} \tag{4}$$

From the linear relation of S to t shown previously and S as a square term in Equation (4), it follows that $\Delta W/W$ should increase linearly with t^2. If the rapid change in work occurring in the short initial phase of ozone attack is neglected, it is found that the work change or cracking effect then proceeds linearly with the square of the time up to the point where stress concentration causes accelerated changes in $\Delta W/W$. A rate expression for cracking effect is derived from Equation (4) by introduction of the squared t term:

$$K = (1/t^2)/(\Delta W/W) = (d\Delta W)/(dtW)$$

$$= (k'S^2/2t^2)1/Z_1 \frac{(L - 1/L^2)}{(L^3 - 3L + 2)/2L} \quad (5)$$

Numerous oxidation reactions exhibit rate constants which are based on the second power of time. It is of interest to note that the cracking effect due to ozone attack appears to fall in the same class. This observation suggests that ozone attack is an oxidation type reaction characterized by extreme rapidity which in general is typical of ozone-olefin reactions.

TABLE XXV

EXTENSION AND CRACKING RATE[a] (BUCKLEY AND ROBISON[95])

L	$K \times 10^9$	Nature of cracking
1.151	0.035	None visible
1.201	0.098	None visible
1.254	0.209	None visible
1.348	0.366	Very small, multitudinous
1.402	0.979	Very small, multitudinous
1.503	2.625	Very small, multitudinous
1.602	2.722	Very small, multitudinous
1.799	2.84	Very small, multitudinous
1.899	16.27	Large, very few
2.000	18.32	Large, very few

[a] GR-I-15 vulcanized 8 minutes at 165° C. Ozone concentration 0.199 vol. per cent in air. Test temperature 25° C.

These authors noted that the effect of extension on the cracking rate constant was not uniform as shown in Table XXV. The data fall into three groups. Up to a stretched length to original length ratio of $L = 1.40$, the cracking rate increase with increased extension was uniform and in the lower range the sample suffered a work change but generated no visible cracks. From this point, up to $L = 1.80$, the effect of increasing L was small. In the range above $L = 1.80$, a few large cracks were formed and these gave rise to inordinately large cracking rate values.

In this work it was also shown that ozonization of the network proceeded without the presence of strain. The strictly chemical part of the mechanism of cracking does not require strain. The mechanical aspects or generation of a sample with new surface in the form of cracks does however require stored energy. The experiment reported in Table XXVI is related to this. It is shown that a sample of butyl vulcanizate can be exposed to ozone for very long times without change in the network structure as indicated by volume swell and weight loss of the sample in the volume swell test. However, when the structure of the sample is opened up by the use of a very efficient plasticizer, degradation is rapid, ultimately ending in complete solubilization of the original

TABLE XXVI

OZONIZATION WITHOUT STRAIN[a] (BUCKLEY AND ROBISON[95])

Sample	Exposure time, hours	% volume swell[b]	% change sample wt.
Pure gum butyl GR-I-15 vulc.	0	519	+0.6
	15	520	+1.4
	30	520	+0.1
	54	518	−2.5
	127	517	−0.8
Pure gum butyl vulc. + 50 phr diisoctyl sebacate	0	605	−28.9[c]
	23	1180	−69.1
	31	Highly degraded	

[a] Ozone concentration 0.200 volume per cent in air. Test temperature 25° C.
[b] Corrected for weight of extractables.
[c] Accounted for by the plasticizer extracted.

three-dimensional network. The prime importance of the permeation of ozone into the sample thus appears evident.

The state of vulcanization and very likely the amount of residual unsaturation has a profound effect on the cracking rate. The results of a study of the chemical unsaturation effects and the extent of vulcanization are described in Figure 78. It is shown that the curves seek a minimum in the cracking rate relative to vulcanization time. The position of this minimum and the allowable range of vulcanization time for low values of the cracking rate are dependent on the chemical unsaturation of the polymer. The nature of these curves sug-

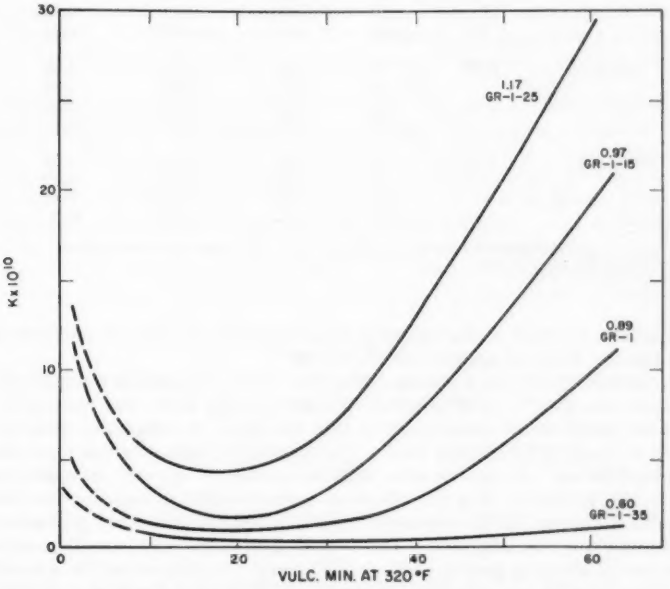


FIG. 78.—Effect of vulcanization time and polymer unsaturation on cracking rate (Buckley and Robison[95]).

gested that reversion at the surface may be present. The research reported in Table XXVII was carried out to examine this possibility. It is shown that although some tendency towards reversion is noted in both the volume swell data and the equilibrium modulus values, the effect admittedly is not very large. However, it should be emphasized that these two properties are dependent on the total volume of the sample while the cracking rate is surface sensitive.

This work tends to place the low permeability of butyl polymers to gases on the same plane as the low chemical unsaturation in controlling the ozone cracking.

A quantitative study of factors operative in the cracking process would appear to have interesting aspects relative to a relatively unexplored area of polymer and elastomer research, namely surface effects. This tendency of

TABLE XXVII

EFFECT OF VULCANIZATION ON CRACKING[a] (BUCKLEY AND ROBISON[95])

Polymer	Mole % unsaturation[b]	Minutes vulcanized at 165° C	Volume swell, %[c]	$Z_1 \times 10^{-6}$ in dynes/cm²	$K \times 10^{10}$
GR-I-35	0.60	8	599	1.125	0.368
		16	533	1.365	0.163
		32	506	1.512	0.190
		60	510	1.533	0.809
GR-I	0.89	8	511	1.446	0.789
		16	456	1.801	0.111
		32	439	1.826	0.130
		60	490	1.777	9.84
GR-I-15	0.97	8	497	1.434	4.88
		16	473	1.699	1.34
		32	446	1.917	3.32
		60	474	1.727	19.4
GR-I-25	1.17	8	445	1.696	5.91
		16	522	2.346	4.12
		32	420	2.162	7.81
		60	465	2.060	29.5

[a] Ozone concentration 0.200 volume per cent in air. $L = 1.25$. Test temperature 25° C.
[b] Method of Rehner and Gray.
[c] Cyclohexane at 25° C.

vulcanizates to crack in the presence of ozone is one of very few sensitive tools available for study of specific surface effects.

A further effort was made to define the effect of plasticizer concentration on ozone cracking[96]. The original objective of this work was related to oil-extended butyl tread compounds so that the type of compound formulation shown in Table XXVIII was used. The plasticizer employed was a petroleum hydrocarbon oil. It can be seen that as plasticizer content increases three effects are produced: (1) the state of vulcanization judged by the elastic modulus decreases, (2) the permeability Q to a test gas (nitrogen) increases and (3) the cracking rate increases. The overall effect of the plasticizer is considered to be one of allowing greater chain mobility and thus increasing the amount of gas (ozone) which can permeate the surface. It should also be noted that the apparent crosslink density would be lower with the higher plasticizer contents.

TABLE XXVIII

OZONE CRACKING OF BUTYL VULCANIZATES AS RELATED TO VULCANIZATION, PLASTICIZER CONTENT, ELASTIC MODULUS AND PERMEABILITY

Plasticizer[a]	0	12.5	25.0	37.5	50.0
$Z_1 \times 10^{-6}$[b]					
30′ @ 307° F	4.89	3.50	2.17	1.85	1.21
45′ @ 307° F	5.05	3.81	2.34	2.02	1.21
60′ @ 307° F	5.57	3.90	3.01	2.05	1.54
90′ @ 307° F	5.52	4.34	3.29	2.25	1.49
$K \times 10^{10}$[c]					
30′ @ 307° F	1.4	14	17	53	167
45′ @ 307° F	1.1	3.3	11	28	138
60′ @ 307° F	3.6	3.9	14	23	56
90′ @ 307° F	1.4	4.7	44	42	72
$Q \times 10^{9}$[d]					
45′ @ 307° F	5.3	6.2	9.9	11.0	12.8

[a] ENJ-B-6 100, HAF 32.5, EPC 32.5, zinc oxide 5, sulfur 1.5, Tellurium diethyldithiocarbamate 1.0, plasticizer, hydrocarbon oil as indicated; times and temperature of vulcanizate are indicated.
[b] Dynes/cm².
[c] Cracking rate, method of Buckley and Robison ($L = 1.25$, ozone conc. 0.2% vol. in air).
[d] Permeability to N_2—$cm^3 \times sec^{-1} \times atmos^{-1}$ at 25° C.

This factor has already been discussed as potentially harmful to the resistance of ozone cracking. The permeability values shown here are inordinately high for the system butyl-nitrogen. Moreover, it would be expected from the work of Van Amerongen that the presence of a large volume of carbon black would further decrease the permeability below that normally associated with the polymer itself. Despite this anomaly, the permeability data show a consistent effect with increased plasticizer content and may be used at least on a relative basis.

Antiozonants, such as N,N′-dioctyl-*p*-phenylene diamine and 6-ethoxyl-1,2-dihydro-2,2,4-trimethylquinoline, have enjoyed considerable succes in SBR polymers. These two materials were added to a tread type butyl compound and furnished the data shown in Table XXIX. The antiozonants are shown to be remarkably effective in butyl even in the presence of high concentrations of plasticizer. It may also be noted that these materials have a significant effect on the state of vulcanization obtained under given conditions.

High energy degradation.—Charlesby[97] discussed the degradation of polymers upon exposure to high energy radiation. Polyisobutene, according to

TABLE XXIX

EFFECT OF ANTIOZONANTS ON CRACKING OF BUTYL VULCANIZATES CONTAINING OIL PLASTICIZER

	Control compound[a]		Compound containing antiozonants[b]	
Plasticizer	$Z \times 10^{-6}$	$K \times 10^{10}$	$Z \times 10^{-6}$	$K \times 10^{10}$
0	5.05	1.10	3.29	0.22
12.5	3.81	3.30	2.49	3.27
25.0	2.34	20.3	1.88	0.69
50.0	1.21	138	0.87	1.52

[a] Same base compound as in Table XXVIII vulcanized 45′ @ 307° F.
[b] N,N′-dioctyl-*p*-phenylenediamine 2 phr, and 6-ethoxy-1,2,-dihydro-2,2,4-trimethylquinoline 2 phr in compounds containing antiozonants.

Charlesby, suffers a reduction in molecular weight under such conditions. The reaction is said to be a main chain breakage followed by rearrangement of effective groups at the points of chain breakage to give stable molecules. Side groups may also be cleaved from the main chain in this reaction. The process is believed to be essentially different from that occurring during thermal pyrolysis. In the high energy process, each chain break occurs independently, no chain reaction being involved, and very little monomer is formed.

In common with other reactions, the chain breakage occurring under high energy conditions is temperature dependent. Although a minor change in energy content results, a relatively small temperature change can markedly affect the amount of chain breakage. Some of the data of Charlesby in this

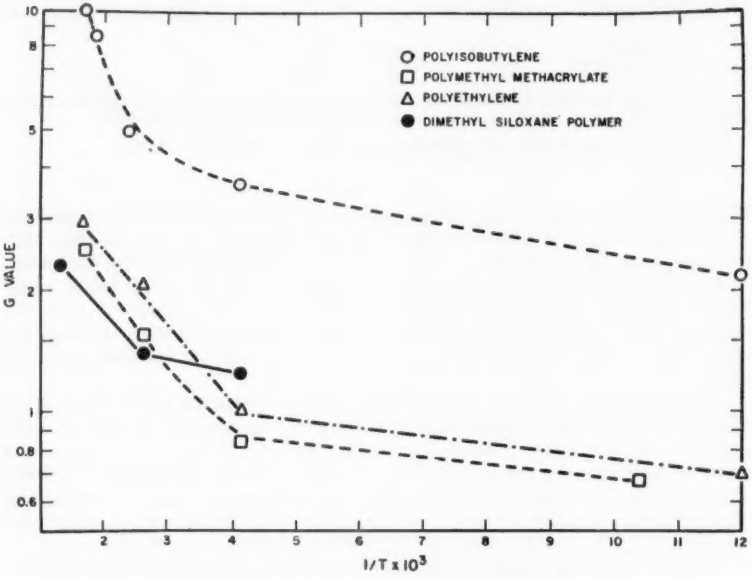


FIG. 79.—Temperature variation of G value (number of main chain fractures or crosslinks per 100 e.v. absorbed (Charlesby[97]).

regard are shown in Figure 79. Here the G value, number of main chain breaks (or crosslinks achieved per 100 e.v. absorbed), is plotted against temperature.

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HIGH TEMPERATURE ELASTOMERIC COMPOUNDS AND POLYMERS

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I. INTRODUCTION

While special purpose elastomers for high temperature applications have been available since the introduction of the polyacrylates and silicones in the early 1940's, the intensive development and study of such materials really began

in the early 1950's. Prior to that period, the major effort in the field of synthetic elastomers was directed toward development of general purpose polymers, principally for such applications as military and civilian tires, wire and cable, and other large volume uses. The extensive synthetic rubber development program sponsored by the U. S. Government during and following World War II is a matter of common knowledge to every rubber technologist and is well covered by Whitby[1]. However, less well known because of restrictions on distribution of reports and technical data are the history and accomplishments of programs sponsored or motivated primarily by the Department of Defense on development of special purpose elastomers for varied and critical high temperature applications.

This review will emphasize current knowledge on these specialty elastomers and will attempt to summarize the general limitations of the more common commercially available elastomers when exposed to high temperature environments. For the reader interested in a comprehensive review of this latter subject, Firestone Tire and Rubber Company[2] prepared an outstanding summary of available information prior to initiating an Air Force sponsored research program on high temperature rubber compounds in 1956.

Arbitrary definition of what constitutes a high temperature elastomer will naturally provide for many areas of controversy. To the metallurgist, organic polymers in general are not considered high temperature materials, yet in certain applications, such as ablation materials for missile nose cones or rocket nozzles, these polymers will exceed the performance of the most advanced alloys, and are actually considered *useful* at temperatures above 4000° F. On the other hand, commercial polymer manufacturers publish volumes of data to show that their particular polymer will withstand prolonged aging periods at temperatures of 200–250° F and thereby claim high temperature performances. Obviously, when considering the entire field of elastomeric polymers, no fine line can be drawn between those which may be considered suitable for high temperature applications and those which should be excluded from such applications.

Further complicating any generalizations regarding high temperature usefulness is the fact that the high temperature environment is rarely the only environment to be considered in any given application for elastomers. Effect of fuels, lubricants, hydraulic fluids, special chemicals, ozone, sunlight, nuclear radiations, and other adverse environments must usually be considered, singly or in combination, along with the heat effects. Finally, in any given application, consideration of a specific physical property, or combination of properties, is essential for satisfactory performance. These properties include, but are certainly not limited to, tensile strength, elongation, stress relaxation, compression modulus, hardness, abrasion, permeability, lubricity, resilience, tear, cut growth, adhesion, and many others which can have a major influence on the performance or service life of an elastomeric component. Control of these properties over a broad temperature range is the real challenge to today's rubber technologists, and the constant broadening of the temperature range, from extremely low (below −300° F) to extremely high (above 1000° F), will continue to be the basis for special purpose polymer and elastomer development in the years ahead.

For purposes of this review, a special purpose high temperature elastomer is defined as an elastomeric vulcanizate which will withstand prolonged aging (500 hours or longer) at temperatures of 350° F or higher in either an air or a fluid environment, but not necessarily in both, and will exhibit a substantial retention of

elastomeric properties, i.e., Shore "A" hardness of 50 to 80, a minimum elongation and tensile strength of 100% and 500 psi respectively, low set at break, and no surface cracking or other evidence of excessive deterioration after the aging period.

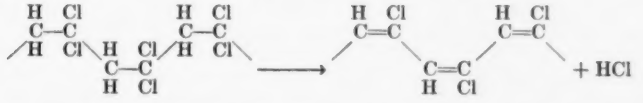
II. TEMPERATURE EFFECTS ON ELASTOMERS

A. DEGRADATION

The performance and usefulness of elastomers at high temperatures is adversely affected by two factors: aging or thermal degradation, and what may be called "reversible" loss of strength and physical properties while at high temperatures.

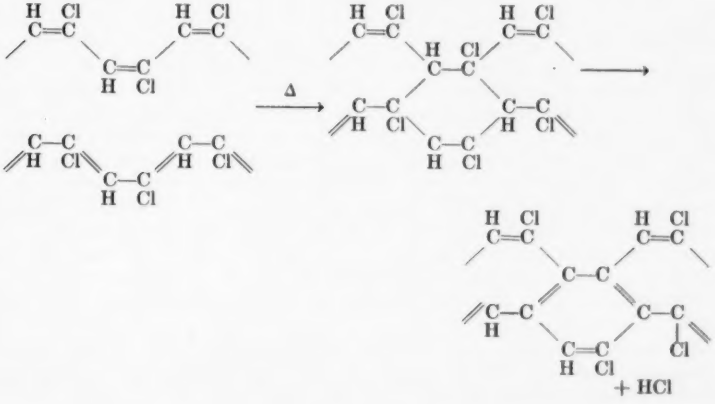
The first factor, thermally induced degradation, may manifest itself in permanent weakening, softening or hardening, embrittlement, or stress relaxation of the elastomer part. This degradation may proceed by one or more of several mechanisms. If the polymer chain breaks into fragments, there are several possibilities[3]. (a) Bonds may be broken at random. (b) Weak bonds, distributed at random in the polymer, may be preferentially attacked. (c) Either (a) or (b) may be followed by an "unzipping" or splitting off of monomer units one by one from an activated end of a broken chain. (d) Reverse polymerization, beginning with an activated chain end (initiation), proceeding with an "unzipping" reaction (propagation), until activation is lost (termination). (e) Some polymers may not undergo scissions in the backbone, but rather suffer bond cleavages between the backbone and side groups. These may be in the form of a "zip" reaction different from those in (c) or (d) in that side groups only are involved. An example of such a reaction might be (1):

(1)



Winslow[4] suggests that such scissions may ultimately result in formation of crosslinks between the chains, perhaps by reaction (2):

(2)



Polymers undergoing degradations of types (a), (b), (c), and (d) would vaporize if heated to sufficiently high temperatures, whereas degradations that are more or less similar to (e) would leave behind a substantial residue. Polymers that are highly crosslinked (vulcanized elastomers and resins) would also leave a large proportion of residue.

Madorsky[5] has reported results of pyrolysis of a number of polymers at various temperatures. Some of his findings are shown in Figure 1.

Depolymerization or crosslinking reactions may be caused or modified by compounding ingredients or by the environment in which the elastomer is heated. Oxygen in the air or in fluids, amines, free-radical decomposition prod-

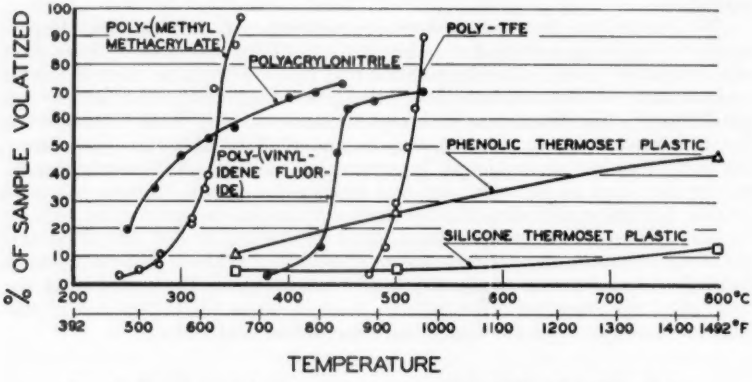


FIG. 1.—Vacuum pyrolysis of representative polymeric materials. From Reference 5.

ucts in fluids or greases, curing agent fragments, or unexpended curing agent in the compound may be active at high temperatures and affect rate or kind of degradation.

B. REVERSIBLE LOSSES

The other factor affecting performance of rubber at high temperature, the reversible loss of physical properties while at high temperatures, has received somewhat less attention than has degradation. Probably the first measurement of the effect of temperature on tensile strength was in 1910 by Breuil[6], who covered a temperature range of from 14° to 212°F. Another early investigation of tensile strengths and elongations at elevated temperatures was by van Rossem and van der Meijden[7], reported in 1926, which included a review of previous work. Their measurements used preheated holders and a mercury bath to bring the ring-shaped test pieces to temperature. Testing over a range of 46° to 300° F, they found the rubber "brittle" at high temperatures, but that the "brittleness" disappeared upon subsequent cooling. Other earlier investigations on Hevea include measurements of the temperature effects on standard stocks[8,9] and studies on the effects of compounding variables on high temperature physical properties by the R. T. Vanderbilt Laboratories. With the advent of GR-S with its high temperature deficiencies, several studies[2] were made comparing high temperature-tensile properties of the commonly available synthetic elastomers—butyl, GR-S, neoprene, nitrile, and hevea, at temperatures up to 284° F.

Kitchen and others at Firestone have compiled as part of another report[2], a list of the articles appearing in the literature up to 1956. This report tabulates previous work and presents graphs comparing tensile *vs.* temperature data obtained in the Firestone study and those obtained by other investigators. Data are given for butyl, GR-S, Hevea, Hypalon, neoprene, nitrile, polyacrylic, and silicone rubbers.

While much data are available on the high temperature properties of elastomers, and more work is currently underway, there is almost nothing to be found on mechanisms of the reversible loss of desirable properties due to heat alone. Van Rossem and van der Meijden pointed to this problem some 30 years ago. The loss of desirable properties may be related to the temperature effect on van der Waals' forces, polymer chain mobility, loss of crystallinity, covalent forces, or the like. It might be hoped that with present understanding of the structure of high polymers, and especially with recent advances in reinforcement theory, those factors determining behavior of elastomers at high temperatures will soon be better understood.

III. LIMITATIONS OF GENERAL AND SPECIAL PURPOSE ELASTOMERS

A. NATURAL RUBBER

Any comparative discussion of the properties of elastomeric materials must certainly include consideration of the natural product. As Fletcher and Fogg[10] correctly point out, the special purpose high temperature elastomers will be slow in finding popularity for such applications as conveyor and transmission belting, certain air and fluid seals, hot water and steam hoses, and high speed tires. The two obvious deficiencies of these special elastomers are high cost and a lack of important physical properties such as elasticity, resilience, and strength.

These authors, under the direction of the Board of the British Rubber Producers' Research Association, are pursuing an aggressive research program directed at obtaining maximum high temperature age resistance in natural rubber compounds through studies of vulcanizing, antioxidant, deactivator, and filler systems. Results of their work indicate that good retention of physical properties of natural rubber stocks may be maintained for as long as 56 days at 212° F and for 14 days at 257° F. The four compounds presented in Table I could form the basis for product compounding for a wide variety of special applications.

While these studies give an indication of the long time usefulness of natural rubber at high temperatures, Smith, F. M.[2] and others investigated the effects of shorter aging periods at higher temperatures. For a typical compound, 25% of original tensile strength was lost in 8 hours at 215° F, and most useful properties were lost in 8 hours at a temperature of approximately 350° F. In this experiment, properties were determined at 73° F after 8 hours at the specified temperature. However, when testing was conducted *at* the aging temperature, loss in properties was somewhat more severe. Results of this work, as shown in Figure 2, provide an excellent indication of the usefulness of natural rubber in applications where strength or elongation at elevated temperatures is essential.

Further studies by Hayes and others[12] of compounding variations showed that some improvement in 8-hour heat aging resistance could be obtained

TABLE I*

FORMULAS OF REPRESENTATIVE NATURAL RUBBER COMPOUNDS

Formula	(1)	(2)	(3)	(4)
Smoked sheet	100	100	100	100
Zinc oxide	25	2	2	—
Stearic acid	2	2	2	—
TMTD	1.5	3	3	—
Tellurium	3	—	—	—
Dicumyl peroxide	—	—	—	3
ZDMDC	—	—	—	3
ZDEDC	3	—	—	—
ZDBDC	—	—	3	—
MBTS	0.5	—	—	—
Lime	—	—	—	2
Flectol H	2	2	2	2
ZMBI	2	—	2	2
Agerite White**	—	1	—	—
FEF black	25	50	50	50
Cure, minutes @ 284° F	30	60	60	60

TMTD—Tetramethylthiuram disulfide
ZDMDC, ZDEDC, ZDBDC—Zinc dimethyl-, diethyl-, and dibutyldithiocarbamates, respectively.
MBTS—2-Benzothiazolyl disulfide
ZMBI—Zinc salt of mercaptobenzimidazole

* Extracted from Reference 10.
** N,N'-Di-2-naphthyl-*p*-phenylenediamine.

through use of antioxidants but that even these materials failed to provide more than marginal improvement in properties when measured at elevated temperatures. Variations in other compounding ingredients including vulcanizing agents, fillers, and even blending with Balata in attempts to maintain

TABLE II*

EFFECTS OF AGING REPRESENTATIVE NATURAL RUBBER COMPOUNDS

Test	Days at 212° F	Formula (see Table I) (1)	(2)	(3)	(4)	Days at 257° F	Formula (3)	(4)
TS	0	2540	3060	2880	2530	0	3240	2540
	28	2080	930	1920	1420	7	1860	1590
	56	950	B	1010	B	14	1070	950
E	0	620	485	470	350	0	440	350
	28	500	285	285	245	7	260	345
	56	370	B	140	B	14	180	230
M100	0	130	270	240	380	0	260	380
	28	190	170	530	370	7	260	230
	56	190	—	630	—	14	240	210
C Set	28	Poor	56	75	78			
	56	Poor	65	81	86			

TS—Tensile strength, psi
E—Elongation at break, per cent
M100—100% modulus, psi
C Set—Compression set at constant strain
B—"Brittle", elongation < 20%

* Extracted from reference 10.

crystallinity failed to produce properties significantly improved over those shown in Figure 2.

While efforts to improve age resistance and high temperature strength of natural rubber will undoubtedly continue, little hope may exist for significant increases in the latter property. According to Kitchen[13], the comparatively high tensile strength of Hevea vulcanizates at room temperature is due in part to crystallinity on stretching. This crystallinity disappears at temperatures above 300–400° F in Hevea and, unfortunately, at even lower temperatures for some of the special purpose high temperature elastomers to be discussed later. In spite of its deficiencies, however, natural rubber or synthetic versions of

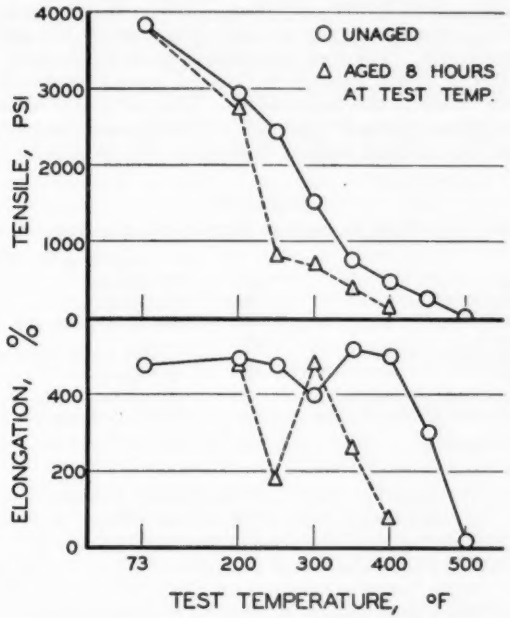


FIG. 2.—Properties of a typical hevea compound when tested *at* high temperatures.

similar structure will continue to be favored for cost and property advantages in many applications.

B. SBR AND MODIFIED POLYMERS BASED ON BUTADIENE

Standard styrene-butadiene rubber (SBR) compounds exhibit the same general order of heat resistance as Hevea. During the investigations previously mentioned, Smith[2] and Hayes[12] found that while SBR compounds had somewhat better retention of tensile strength after 8 hours at 250° F, loss of elongation in the 300–350° F range was excessive. Also, compounding variations had little effect on improvement of strength *at* temperature.

However, during the course of their investigation of high temperature re-

sistant rubber compounds, a significant advance in polymers exhibiting superior strength at temperature was made. Extensive compounding and evaluation studies of all commercially available elastomers had demonstrated that the maximum tensile strength obtainable when testing was conducted at 400° F was less than 800 psi. Therefore, efforts were directed toward modification of known structures through introduction of functional groups which could enable the polymers to be cured by new techniques. Early work on polymers containing carboxyl groups demonstrated the feasibility of improving 400° F tensile strength through the use of special curing systems. However, the carboxyl-containing elastomers were difficult to process and would not have been practical for commercial applications. Therefore, emphasis was shifted to a 70:30 butadiene-methyl methacrylate copolymer. Attempts were made to hydrolyze a portion of the methacrylate ester at curing temperatures through use of metal oxides and hydroxides. The most successful experiment produced an elastomer exhibiting a 400° F tensile strength of 1760 psi, more than double that of any other elastomer tested at this temperature. This methacrylate rubber with its special curing system, shown in Table III, exhibited 8-hour heat aging resistance comparable to other general purpose elastomers, but, as is to be expected, was

TABLE III

PROPERTIES OF A 70:30 BUTADIENE–METHYL METHACRYLATE COPOLYMER

		Unaged properties @ 73° F	
Polymer	100	Tensile, psi	3425
$Ba(OH)_2 \cdot 8H_2O$	20	Elongation, %	230
Barium oxide	10	200% modulus, psi	3225
HAF black	40		
Epon 828 resin*	5	Unaged properties @ 400° F	
Pine tar	5	Tensile, psi	1760
N-phenyl-2-naphthylamine	2	Elongation, %	370
Optimum cure @ 320° F, min	30	200% modulus, psi	990

* Shell Chemical Company.

quite inferior to the special purpose high temperature elastomers in this respect. It should also be noted that further work on this system produced elastomers with reproducible strengths of slightly less than 1000 psi at 400° F. While the commercial future of such elastomers is in doubt, the encouraging results obtained do provide the incentive necessary to continue the search for elastomeric materials exhibiting a good balance of physical properties at high temperatures.

Another recent development involving modification of diene polymers has been disclosed by Meyer, Pierson and others[14]. Highly saturated methyl mercaptan adducts of emulsion polybutadiene were prepared and their high temperature aging resistance, and other special properties, compared with those of commercially available general purpose elastomers[15]. These adducts were prepared by the addition of methyl mercaptan to the unsaturated bonds of polybutadiene by a free radical chain process with the reaction being carried out in latex medium. The most heat resistant vulcanizates were prepared using hydrated lime and dicumyl peroxide to effect the cure. Based on the limited physical property data available at the time of this writing, it would appear that the adduct elastomers exhibit a reasonable balance of original properties and are definitely superior to standard SBR in heat aging resistance, However, based on loss of properties in the 300–500° F temperature range, they definitely cannot be classed as special purpose high temperature elastomers of the silicone

or fluorocarbon type. Whether the combination of possible low cost, ozone resistance, radiation resistance, and other special properties will make these elastomers attractive for commercial applications is a matter of doubt at the present time.

C. BUTADIENE-ACRYLONITRILE COPOLYMERS (NBR)

In discussing applications for NBR compounds, it is not possible to limit consideration to the single environment--heat. Virtually all uses for NBR compounds involve fluid retention, thus requiring that investigation of fluid resistance be conducted over the temperature range dictated by the end application. While numerous important commercial uses for NBR exist, the authors are more familiar with the essential and, in many instances, vital applications of NBR in military aircraft and other weapons systems. Therefore, a brief review of the intensive research directed toward improving high temperature capabilities of these elastomers should provide an indication of their current limitations.

There is little doubt that the outstanding performance and reliability of modern commercial or military aircraft would not be possible without high quality NBR compounds or their equivalent. The excellent fuel, oil, and hydraulic fluid resistance of these elastomers, over a relatively broad temperature range, combined with other essential elastomeric properties has resulted in their widespread application in such components as hose, "O"-ring seals, gaskets, fuel cells, diaphragms, and many others. Frequently, these components are so critical to the performance of an aircraft or missile that their failure could result in catastrophic destruction of the vehicle. Since, to date, attempts to completely eliminate elastomeric materials from aircraft fluids systems have been unsuccessful, the reasons for intensive research to extend the capabilities of, or find replacements for, NBR compounds becomes apparent.

Extensive compounding of NBR elastomers to upgrade their physical properties has been done by the commercial suppliers of the basic polymers. Comments on these compounding studies conducted by U. S. polymer producers, including Goodrich, U. S. Rubber, Goodyear, and Firestone, or by the various foreign manufacturers, are not considered pertinent to this review. In general, the majority of high temperature evaluations were conducted in the 200–250° F range since until very recent years, this range was most applicable to automotive and aircraft applications.

However, in the early 1950's it became apparent that higher performance in aircraft engines would result in higher temperatures being generated within their lubrication systems. Indications were that these higher operating temperatures would necessitate major changes in types of lubricants to be employed, and fluid development was therefore directed away from the conventional petroleum base oils into the area of synthetic fluids, with emphasis on esters and diesters. This introduced a new adverse environment in addition to elevated temperatures in which elastomeric materials were required to perform.

Early work by Byerley[16] indicated that high acrylonitrile NBR compounds had satisfactory fluid resistance, but exhibited surface cracking after relatively short immersion periods in synthetic fluids at temperatures above 250° F. Since a 350° F target had been established by aircraft engine manufacturers, it was obvious that considerable research would be required to obtain suitable elastomers for high performance engines then under development. Toward

this end, an Air Force contract was placed with the Battelle Memorial Institute for study and development of high temperature oil resistant elastomers with emphasis on NBR compounds. Since the contract objective was to study long term (up to 1000 hours) exposure at 350–550° F, this program, which continued for approximately three years, represents what is probably the most intensive effort to obtain maximum high temperature performance from such compounds. The three technical reports[17–19] published during this period include very comprehensive coverage of the effects of curing systems, fillers, antioxidants, plasticizers, and other ingredients on high temperature behavior of NBR.

Early work centered on evaluation of conventional and experimental compounding ingredients in attempts to inhibit degradation of nitrile type compounds at 350° F. Commercial manufacturers' literature indicates that significant effects on heat resistance to 250° F can be made through selection of compounding ingredients, but the work of Gillen and others[17] showed that regardless of curing system employed, properties after 168 hours aging at 350° F in typical diester fluids were quite similar. Likewise, studies of a wide variety of commercial and experimental antioxidants, even at concentrations up to 10–20 phr, failed to provide any significant increase in 350° F aging resistance. Similar studies of plasticizers, curing conditions, and other variables were also fruitless. However, two factors were shown to have a significant effect on aging characteristics in the temperature range under investigation. Normal to high (40–80 phr) loadings of carbon black contributed to inferior aged properties and increased cracking of aged stocks when flexed. Also, as had been previously observed by Byerley[16], the best balance of oil resistance and aging qualities was obtained with butadiene-acrylonitrile copolymers containing 40 to 45 per cent acrylonitrile.

Intensive investigation of non-black fillers resulted in a composition containing 100 phr of magnesium oxide which, based on physical property determinations, appeared to represent a significant "break-through" in NBR compounding. Conventional black loaded compounds had been generally found to exhibit a tensile strength of less than 1000 psi after 168 hour oil aging at 350° F. However, the early magnesia loaded compounds exhibited strengths of over 2000 psi after the same aging. The outstanding aging characteristics of these compounds were further confirmed by Mueller[18], and Clark and Gillen[20], who demonstrated that a reasonable balance of properties was maintained after 500 hours of fluid aging at 350° F as shown in Table IV.

This recipe represents one of the best high temperature NBR compounds produced but, while of considerable interest to compounders, has not found wide spread military or commercial applications because cracking after high temperature exposure has not been overcome, and these magnesia filled compounds are extremely difficult to process and otherwise adapt to commercial production.

Nevertheless, these compounds have formed the basis for further studies by other investigators concerned with high temperature fluid resistance. Fujiwara, Spain, and Smith[21,22,23], working under Air Force contract at Wyandotte Chemicals Corporation, confirmed the fact that white fillers in NBR compounds provided heat resistance superior to that obtained with carbon black in such compounds. Aluminum oxide, hydrated sodium silico-aluminate, hydrated calcium silicate, hydrated silicon dioxide, and calcined magnesium oxide were found to give the best properties after aging in jet fuels and other aromatic test fuels. Retention of properties after high temperature fuel aging are also

shown in Table IV for the magnesia filled NBR compound, and represent significant improvement over conventional compounds.

For short duration high temperature fuel service, another interesting NBR compound based on a peroxide curing system was investigated and found to have reasonable retention of physical properties and low volume increase, after 400° F aging, Table V.

In aircraft hydraulic systems, NBR compounds are put to their most severe test. For many years serviceability over a temperature range from minus 65° F to plus 160° F has been required, with operating pressures to 3000 psi. The most critical component is, of course, the common "O"-ring seal, and the attainment of desired performance and reliability requires an extremely high quality NBR compound. With the advent of the first generation of supersonic aircraft, it became necessary to raise the maximum operating temperature limit of hydraulic seals and other elastomeric components to 275° F. Attempts to obtain NBR compounds serviceable over this new temperature range from

TABLE IV

PROPERTIES OF A MAGNESIA–FILLED NBR COMPOUND

Hycar 1001	100
Zinc oxide	5
Stearic acid	1.5
Sulfur	0.5
Methyl Tuads (TMTD)	0.25
Thioglycolic acid	5.2
Flectol H*	3
Magnesia ELC	100
Cure 60 min @ 310° F	
Original properties	
Tensile strength, psi	2460
Elongation, %	610
Hardness, Shore A	77
Aged in diester base engine oil 500 hrs. @ 350° F	
Tensile strength, psi	750
Elongation, %	80
Hardness, Shore A	85
Volume swell, %	16
Cracking	Cracked
Cure 90 min @ 310° F	
Original properties	
Tensile strength, psi	1890
Elongation, %	350
Hardness, Shore A	80
Aged in ASTM Reference Fuel "B" (70/30 isooctane/toluene) 500 hrs. @ 325° F	
Tensile strength, psi	2150
Elongation, %	155
Hardness, Shore A	65
Volume swell, %	20

* Monsanto Chemical Company.

minus 65° F to plus 275° F have been moderately successful, but there is little doubt that some sacrifice has been made in service life in the higher temperature systems.

In summary, therefore, we find that suitably compounded NBR elastomers may be successfully employed in some fluids systems in the temperature range 250–350° F. In general, however, application above 250–275° F is not recommended for dynamic applications because of the surface cracking which is encountered after fluid immersion. At temperatures above 275° F, it has been observed that this cracking can frequently be attributed to oxidation products forming in the fluid and not to any direct high temperature effect on the elastomeric compound[24].

Actually this surface cracking has caused considerable difficulty in obtaining reproducible results in laboratory testing. Murray[25] observed that at temperatures above 275° F, standard ASTM test procedures are no longer adequate. He conducted an extensive investigation of the variables encountered in the testing of elastomers at high temperatures, particularly in the synthetic lubricants. Variables investigated included testing techniques, oil to rubber ratio, oil-air contact, batch to batch variations in oil samples, and other factors which

TABLE V

PROPERTIES OF A DICUMYL PEROXIDE CURED NBR COMPOUND

Hycar 1041	100
Aluminum oxide (Alon C)*	101
Dicumyl peroxide	2

Cure 90 min @ 310° F

	Original properties	Aged in ASTM Reference Fuel "B" (70/30 isooctane/toluene) 70 hrs @ 400° F
Tensile strength, psi	4590	1570
Elongation, %	360	60
Hardness, Shore A	88	87
Volume swell, %	—	16.8

* Godfrey L. Cabot, Inc.

could influence test results. Results of these studies indicated that unless care was taken to insure convection currents within the test oil sample, oxidation of the oil began at the surface and progressed downward at a rather slow rate. The oxidation products forming in the oil then attacked the elastomer specimen in a non-uniform manner resulting in non-reproducibility of results during laboratory testing. It was therefore recommended that a chimney-stoppered test tube method, in conjunction with an aluminum-block heater or an oil bath, be employed for eliminating many of the variables encountered. This procedure is particularly applicable to evaluating elastomers in engine oils or other fluids where air to oil contact may be expected in actual service. Naturally, for hydraulic fluids and fuels, very high temperature aging in completely sealed containers is essential, and has been found to yield reasonably reproducible results. However, in any discussion of high temperature elastomers, importance of test procedures cannot be over-emphasized. Some investigators have been misled by good results of tests in which the fluid was not exposed to sufficient air. Aging devices and techniques become increasingly important as temperatures pass 300° F and are found to be quite critical in the 500–600° F temperature range.

D. NEOPRENE

While little information is available in technical journals or manufacturers' literature on the heat aging of neoprene compounds above the temperature range of 212–250° F, there is little doubt that such compounds are successfully employed at temperatures above this range. During the investigation at Firestone mentioned earlier, Hayes and others[12] found that neoprene had a higher tensile strength *at* 350° F than any other elastomer tested. However, above 350° F the tensile strength of the neoprene dropped rapidly, and, of course, presently available neoprene compounds have poor resistance to heat aging at 350° F. Surprisingly, properly compounded neoprene elastomers have provided the interim successor to NBR compounds in high temperature aircraft hydraulic system applications.

It had been known for some time that as hydraulic system temperatures exceeded 300° F, conventional petroleum base hydraulic fluids would no longer be adequate. Therefore, Air Force sponsored research led to the development of a non-petroleum base hydraulic fluid which appeared to meet all of the require-

TABLE VI

PROPERTIES OF A NEOPRENE COMPOUND

		Original properties	
Neoprene WRT	100		
Zinc oxide	2.5	Tensile strength, psi	1720
Magnesium oxide	4	Elongation, %	200
NA-22	1	Hardness, Shore A	64
Butyl oleate	15		
MT black	40		
SRF black	40		
		Aged in closed test tubes, 85:15 MLO 8200/Plexol 201 168 hrs @ 400° F	
		Tensile strength, psi	650
Cure 20 min @ 310° F		Elongation, %	85
		Hardness, Shore A	63
		Volume swell, %	22
		Brittle point, ° F	−57

ments for a minus 65° to plus 400° F fluid. This fluid, originally designated as MLO-8200, was based on disiloxanes which were found to be very detrimental to NBR compounds. Their action was that of hardening and shrinking rather than excessive swelling as is normally encountered. After extensive studies, Kitts[26] found that neoprene base elastomers were most resistant to such fluids, but that even they exhibited excessive shrinkage. Through cooperative efforts of the rubber technologists and the fluid chemists, a unique solution to this problem was found. It was observed that the addition of 15 per cent of a diester, such as di-2-ethylhexyl sebacate, to the disiloxane base hydraulic fluid would not adversely affect fluid properties and had a definite beneficial effect on high temperature aging properties of neoprene compounds. Addition of the diester to the base fluid also gave a considerable increase in the low temperature performance of these compounds, an essential property in aircraft hydraulic system applications. To demonstrate this the compound shown in Table VI exhibits a reasonable balance of elastomeric properties after periods as long as 168 hours at 400° F in a blend of the MLO-8200 and 15 per cent Rohm & Haas Co. Plexol 201. Even after the 400° F aging period, this compound retains a low brittle point.

Using these data as a starting point, commercial manufacturers have produced suitable neoprene compounds which are successfully employed in this nation's first supersonic bomber, the Convair B-58. While application of neoprene at 400° F is not generally recommended, this example indicates how high temperature performance may sometimes be obtained through cooperation of the rubber technologist, fluid chemist, and design engineer.

E. BUTYL

Elastomers based on butyl polymers (see the preceding review, this issue) most certainly deserve serious consideration when exposure to moderately high temperature is involved. Widespread application of butyl compounds in such products as tire curing bags, diaphragms for "Bag-O-Matic" presses, steam hose, and others indicates the superiority of these elastomers over other available general purpose polymers for important industrial applications.

This attractiveness of butyl is based on the fact that the elastomer tends to soften rather than harden and embrittle as do many other elastomers when

TABLE VII

TWO BUTYL COMPOUNDS

	S1	R8
Enjay Butyl 215	100	100
Sulfur	2	—
TMTD	1.25	—
MBTS	0.5	—
Zinc oxide	5	—
Stearic acid	0.5	—
Super Beckacite 1001*	—	8
$SnCl_2 \cdot 2H_2O$	—	2
Plasticizing oil	5	5
HAF black	50	50
Cure 60 min @ 322° F		

* Believed to be a condensation polymer of *p-tert*-butylphenol and formaldehyde. A product of Reichold Chemicals, Inc.

heated in an oxidative atmosphere. As Thomas and Sparks[27] point out, numerous mechanisms for the oxidative degradation of butyl have been proposed, but it is generally accepted that methyl side groups on polymers of low unsaturation tend to favor chain scission or reversion and softening, whereas in polymers containing a high proportion of double bonds, often the crosslinking reaction predominates, and the elastomers harden.

Recently, the attractiveness of butyl for high temperature applications has been even further enhanced through disclosure of curing systems for the vulcanization of butyl rubber by phenolic resins. Tawney, Little, and Viohl[28] have presented data which indicate that such vulcanizates exhibit an upper limit of serviceability which is approximately 100° F higher than that obtainable through sulfur or other curing systems. Also, excessive reversion or softening at the high temperatures is greatly reduced. To illustrate this, they prepared a typical sulfur cured compound which they designated as formula S-1 and compared its resistance to high temperature air aging with a phenolic resin cured compound (Table VII).

The addition of stannous chloride dihydrate to formula R8 (Table VII) not only accelerates the cure but increases the overall state of cure obtainable. The

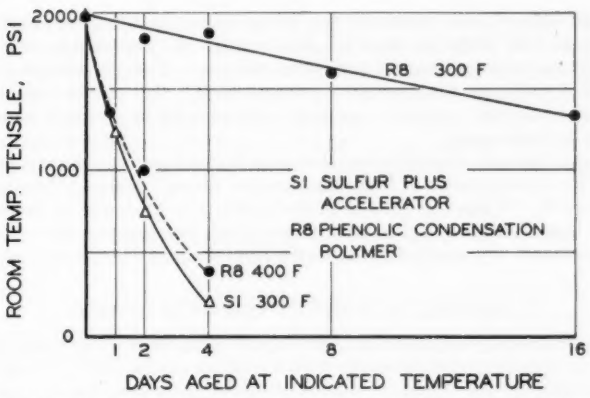


FIG. 3.—Comparison of high temperature properties of a resin cured butyl compound with those of a sulfur cured compound. From Reference 28.

high temperature aging resistance of formula R8, as presented in Figure 3, indicates that this upgrading of butyl elastomers almost places them in a class with the special purpose high temperature elastomers.

Further confirming the superior high temperature resistance of butyl compounds cured with phenolic condensation polymers are the results obtained by

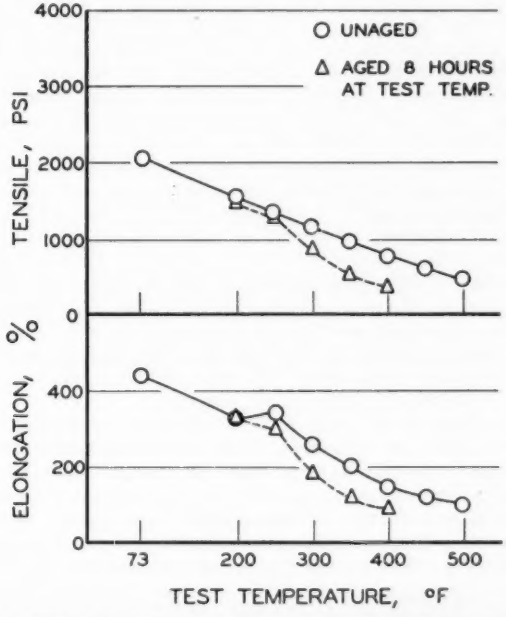


FIG. 4.—Effect of elevated temperature testing on a resin cured butyl compound.

Smith and others[2] who measured the properties *at* high temperature of elastomers cured with Rohm & Haas Co. Amberol ST 137, reported to be a condensation polymer of *p*-octylphenol and formaldehyde. Their results, as presented in Figure 4, indicate that specially compounded butyl stocks exhibit useful retention of physical properties at high temperature in addition to excellent resistance to heat aging.

This combination of properties led to selection of butyl rubber as a promising material for development of high temperature aircraft tires by two Air Force contractors[2,29]. While the success of their efforts is in doubt at present, it is expected that further marginal increases in high temperature performance of butyl elastomers will result from investigation of other vulcanizing agents.

F. MISCELLANEOUS SPECIAL PURPOSE ELASTOMERS

The commercially available special purpose elastomers which may occasionally find applications at moderately high temperatures include the polysulfides, as represented by the Thiokol* solid and liquid polymers, the polyurethanes, and the chlorosulfonated polyethylenes, as represented by Hypalon** 20. Of these elastomers, only the latter may be considered to have outstanding heat resistance as compared to natural rubber or neoprene. Manufacturer's literature[30] shows that properly compounded Hypalon retains elongations in excess of 100 per cent after two weeks continous aging at 300° F. This retention of elastomeric properties after high temperature exposure, combined with other desirable characteristics, has resulted in widespread acceptance of the elastomer by the automotive industry for such applications as spark plug boots, ignition wire, and others[31]. Obviously, the price advantage of this polymer over the special purpose high temperature elastomers is responsible for this acceptance.

The polysulfide elastomers which should certainly rate first choice for resisting nonpolar fluids, have not, unfortunately, been successfully modified to possess outstanding high temperature capabilities. Aside from the propellent field, the most critical military application for these elastomers is in the sealing of integral fuel tanks of aircraft, and for a number of years the polysulfide sealants have been used in continuous service at temperatures to 180° F for this application. When requirements for higher temperature performance were imposed, the commercial sealant compounders directed their efforts toward upgrading the heat resistance of polysulfide polymers through studies of curing systems. One partially successful system employed soluble bichromates or chromates instead of the conventional lead dioxide curing agents[32]. This resulted in an increase of approximately 100° F to the high temperature limit along with increased resistance to fuels and special chemicals. Further work based on this system resulted in practical polysulfide base sealants useful over the temperature range of minus 65° F to plus 275° F, a range far short of the requirements of advanced supersonic air weapons.

The urethane rubbers form one of the most attractive families of elastomeric materials to appear on the commercial market in recent years. The wide range of mechanical properties which can be obtained, combined with their versatility in production of finished items, has attracted considerable interest in these elastomers for a wide variety of commercial applications. Unfortunately, however, these interesting materials can not, as yet, be considered as high temperature elastomers. Kittner and Pigott[33] pointed out in 1957 that urethane

* Reg. T. M., Thiokol Corporation.
** Reg. T. M., E. I. duPont de Nemours & Company.

rubbers "may be used in dry air continuously at 180° F, for some days at 212° F, for several hours at 270° F, and for some minutes at 300° F". More recent developments by Pigott and others[34] indicate that temperature limitations may be extended to 400° F through careful choice of crosslinking systems, but time-temperature data are not presently available. There is little doubt that intensive efforts will be continued by a number of manufacturers to upgrade the high temperature performance of the urethane elastomers and thereby greatly increase their versatility.

IV. THE SEARCH FOR SPECIAL PURPOSE HIGH TEMPERATURE ELASTOMERS

Since one of the principal objectives of this review is to discuss the development and properties of the special purpose high temperature elastomers, as defined in Section I, it was felt that a brief summary of the interesting history leading to the introduction of these materials would be pertinent.

A. ACRYLATE AND POLYACRYLATE ELASTOMERS

The earliest work in acrylate rubbers was probably done by the German chemist, Otto Rohm, who took out patents in 1912 for an "artificial acrylate rubber". His "curing" system employed sulfur at a moderate temperature, which probably did not actually vulcanize this type of rubber. From then until the 1940's, one finds rather few articles in the literature.

In the 1940's, the Eastern Research Laboratories of the U. S. Department of Agriculture began work on useable acrylate rubbers. The work of Mast, Fisher, Dietz, Smith, and Rebberg and others[35,36,37] resulted in the introduction of the "Lactoprene" rubbers in 1943–44.

The first Lactoprene EV was a copolymer of ethyl acrylate with 5 per cent chloroethylvinyl ether to provide curing sites. This rubber had good heat and fluid resistance, but poor low temperature and water resisting properties; a butyl acrylate/acrylonitrile copolymer, Lactoprene BN 12.5, was developed to overcome these two deficiencies[38].

The B. F. Goodrich Chemical Company then introduced Hycar PA and Hycar PA-21 (now Hycar 4021) in 1948. Monomer-Polymer, Inc. (now a division of Borden Company) later produced Acrylon BA-12, and Acrylon EA-5.

Early compounding studies[36,38,40] on the polyacrylates led to practical curing systems based on peroxides, quinone dioxime, and basic oxides. Several investigators[38,39] noted the outstanding heat aging properties of these elastomers from tests conducted in air and fluids for 28 days at 300–350° F. A detailed literature survey on this family of elastomers was completed by Gillen and others[17] during the course of Air Force sponsored research previously mentioned.

B. SILICONE ELASTOMERS

A comprehensive review of the history of silicone elastomers would require tracing the history of silicon chemistry from the time this element was first isolated by Berzelius in 1824, up to present day knowledge of organo-silicone chemistry. Since a review of this type has already been completed in a very excellent manner by McGregor[41], only a few significant facts directly related to silicone elastomers are presented here.

Between 1900 and 1940, one outstanding investigation of the chemistries of carbon and silicon was carried out by F. S. Kipping of the University of Notting-

ham in England. Although he was interested in the chemistry of silicon, *per se*, he investigated the organic derivatives of silicon as the most promising route toward new knowledge in this area. Among his many contributions were the use of the Grignard reaction to prepare silicones, the discovery that no two groups on the same silicon atom ever react together, that silicon and carbon will not form a double bond, and many others.

A little before 1940, the Corning Glass works engaged Dr. J. F. Hyde to investigate possibilities in inorganic-organic polymers. He was able to show that silicone resins exhibiting good heat resistance could be made, and fairly intensive research on such materials was begun. Later this work on insulating resins and the technology of their production was continued under the Corning Glass Works Fellowship at Mellon Institute under McGregor[41].

Work on silicone polymers in a variety of forms reached the point that commercial production could be considered. The Dow Corning Corporation was formed and was in commercial production of organo-silicone oils and antifoam agents in 1943.

The General Electric Company had also initiated a study of organo-silicone insulating resins under Rochow and Patnode[42] and results of their findings eventually led to a family of silicone products. In 1945, both Dow Corning and General Electric announced development of silicon elastomers and General Electric opened its plant for production of silicone products.

Continued developments by both of these organizations, and by Union Carbide, have resulted in the availability of methyl-phenyl and methyl-phenyl-vinyl types of silicone rubbers, the latter permitting improved curing systems and better compression set characteristics. Other advances have been the use of fumed silica fillers, the development of fluorinated fluid resistant silicone rubbers, the history of which is discussed elsewhere in this article, and the recent development of nitrile- or cyano-silicone rubbers having fluid resistance.

C. FLUORINE-CONTAINING POLYMERS

Most of the fluorine-containing special purpose high temperature elastomers available today are the direct result of research conducted or sponsored by the Department of Defense. However, to state that these materials were the result of a planned search for high temperature polymers would be completely erroneous since original polymer development programs were directed toward low temperature, fuel resistant materials.

In the late 1940's the U. S. Air Force was plagued with an epidemic of fuel leakage on many of its aircraft. So critical was this problem that serious consideration was given to the grounding of the entire bomber fleet until at least a temporary solution was found. Briefly, this leakage resulted from the introduction of aircraft fuels of low aromatic content which caused less swell of the seals and other elastomeric components in fuel systems. The effect of this decreased swell was two-fold. Extraction of plasticizers from the NBR compounds used was not sufficiently compensated for by swell of the polymer in the low aromatic fuel, and net shrinkage of the elastomer part resulted. Also, loss of low temperature plasticizers without replacement by fuel, which in itself is a good low temperature plasticizer, greatly aggravated the leakage problem when low temperatures were encountered by the aircraft.

A temporary solution to this problem was found through installation of new seals and other components of the same composition as previously used and through procurement of only fuels containing a specified minimum aromatic

content. The permanent solution to low temperature leakage was believed to lie in the development of new fuel resistant elastomeric polymers which would not require plasticizers to obtain low temperature performance.

Therefore, in May of 1949, a contract was placed with the Minnesota Mining and Manufacturing Company to investigate synthetic rubbers from carbon-fluorine compounds. This approach was considered sound since it was known that replacement of a major portion of the carbon-bonded hydrogen atoms in organic compounds by fluorine atoms produced compounds having greatly increased stability to chemical attack and decreased solubility in ordinary solvents[43]. Further, it was recognized that the two commercially available highly fluorinated polymers, polytetrafluoroethylene and polytrifluorochloroethylene, did possess low temperature "flexibility". Selection of Minnesota Mining and Manufacturing Company for this research was based on their possession of an electrochemical fluorination process invented by Professor J. H. Simons[44]. This process was considered essential for preparation of many of the flourochemicals required for polymer studies.

The first year of this program was devoted to preparation of monomers of high fluorine content. Several classes of such monomers were prepared, including completely fluorinated olefins, mixed fluorocarbon-hydrocarbon olefins, the vinyl esters of fluorocarbon acids, the acrylate esters of fluorocarbon alcohols, perfluoroacrylonitrile, and perfluoroimines. The following two years' effort was directed toward polymerization studies with these materials or others as they were prepared. During this three year period, the esters of acrylic acid with 1,1-dihydroperfluoroalkylalcohols represented the most promising class of monomers from which to prepare rubbery polymers and copolymers. The homopolymers of 1,1-dihydroperfluoro-alkyl acrylates, from the ethyl through the decyl members for alkyl groups containing an even number of carbon atoms, were prepared and studied[45]. Most intensive investigation was made of poly 1,1-dihydroperfluorobutyl acrylate (Poly-FBA), which exhibited the best balance of physical properties combined with a high degree of resistance to swelling by fuels and oils. Unfortunately, this polymer had a brittle point of between 0° and minus 20° F.

However, during this period, discussions within the Air Force and the aircraft industry began to emphasize problems anticipated in the era of supersonic flight which was fast approaching. In any discussion of organic materials, including fluids, plastics, and elastomers, the high temperature environment was considered the most serious obstacle to development of vehicles having the desired performance. Since temperatures of 300–600° F were predicted for many critical aircraft components of the 1955–1960 time period, it became obvious that intensive materials development would be required. With this objective in mind, Hamlin[46], at Wright Air Development Center, found that properly compounded Poly-FBA exhibited high temperature fluid resistance not obtainable from any other polymer then commercially available.

Therefore, during the fourth year of this research program at Minnesota Mining and Manufacturing Company, the additional objective of developing elastomers suitable at 350° F or higher was included[47]. This effort to develop high and low temperature fluid resistant elastomers from carbon-fluorine compounds continued until 1957 and yielded many valuable contributions to the fields of fluorine and polymer chemistry[48]. A useful polymer, Poly-FBA, later known as 3M Brand Fluoro-Rubber 1F4, was developed which provided an interim solution to a number of critical elastomer problems in high temperature hydraulic and engine lubrication systems. Also, an additional polymer, poly

3-perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate, later known as 3M Brand Fluoro-Rubber 2F4, was developed which exhibited a minus 37° F brittle point, with little sacrifice in high temperature performance. High manufacturing costs and subsequent development of superior polymers prevented the production of this latter elastomer on even a significant pilot plant scale.

At the time the Air Force was sponsoring investigation of fluorocarbon polymers with emphasis on fluoroacrylates, the U. S. Army, because of an urgent need for low temperature fluid resistant elastomers, also initiated research in this area with emphasis on polymers and copolymers of fluoro-olefins and chlorofluoro-olefins. This work, under direction of the Quartermaster Corps, was undertaken at the M. W. Kellogg Company and had as its objective the development of a fluorine-containing fuel and oil resistant elastomer which would retain rubbery properties between minus 70° F and plus 160° F. In many respects, this program followed a pattern similar to that of the Air Force program. The first three years' effort covering the period July 1950 to July 1953[49] produced many significant results and valuable contributions to the fields of fluorine and polymer chemistry, but failed to satisfy the original contract objectives. During this period, a broad investigation, which included monomer synthesis, polymer preparation, and evaluation of rubbery polymers, produced 361 fluorocarbon based copolymer systems of which 147 yielded rubberlike materials.

Of these systems, the one which produced a commercial product of considerable importance in a number of critical military applications was the system based on copolymers of chlorotrifluoroethylene and vinylidene fluoride (CF_2=$CFCl$/CF_2=CH_2). Interesting rubbery copolymers were obtained from this system over a wide range of copolymer compositions, with the most promising materials being found in the 30 to 55 mole per cent CF_2=$CFCl$ range. However, early studies of cured stocks indicated that the 30:70 molar ratio provided the best balance of oil resistance and low temperature flexibility, with the latter property falling far short of that desired in an "arctic rubber".

Nevertheless, these copolymers were found to exhibit excellent resistance to corrosive chemicals, such as fuming nitric acid, and this factor alone was sufficient to warrent intensive investigation of both the copolymer system itself and vulcanizing techniques for producing useful elastomers. During these studies, the polymers were designated as X-300 rubber. The majority of the compounding studies on this rubber, and other polymers resulting from the contractual effort, were conducted under the direction of C. B. Griffis[50] of the Quartermaster Corps. The first practical cures for X-300[51] were based on organic diisocyanates, and extensive evaluation of these agents was undertaken. It was later found that useful vulcanizates could also be obtained with either peroxides or amines. Results of such studies confirmed the excellent resistance of these elastomers to corrosive chemicals, and product development of such items as protective clothing, gloves, footwear, gaskets, and other items were undertaken by the Army. In early 1955, the M. W. Kellogg Company provided its own support for the pilot plant production of X-300 rubber and shortly thereafter introduced the commercial product known as Kel-F Elastomer*.

During the course of a routine investigation of Kel-F Elastomer, Headrick[52] found that in addition to chemical resistance, properly compounded stocks exhibited outstanding resistance to experimental hydraulic fluids at temperatures to 400° F. Since, as previously mentioned, high temperature resistance was

* Reg. T. M., M. W. Kellogg Company. The Kel-F Properties were purchased by Minnesota Mining and Manufacturing Company in 1958.

then being emphasized in Air Force polymer development programs, these findings led to an even closer working relationship between the Air Force and Army in the polymer development and evaluation area. Therefore, in late 1954, the scope of the Kellogg program was expanded to include development and evaluation of fluorine-containing elastomers stable to 500° F[51]. The enlarged scope of this program resulted in early recognition of the system which has since provided a very important polymer for high temperature applications—the vinylidene fluoride–hexafluoropropylene copolymer system.

While the monomers for preparation of this copolymer had been available since very early in the program[49], the first serious attempts to study this system began in late 1954 and early 1955. It was then noted[52] that rubbery products could be obtained in good yield and that some of these products retained original rubbery characteristics after 100 hours at 500° F and even after an additional 21 hours at 600° F. Vulcanizates of the copolymer were prepared and found to exhibit a good balance of original physical properties combined with resistance to high temperature aging in diester lubricants.

Following these observations, a number of exploratory copolymerizations using similar monomer systems were conducted[54]. However, none of these yielded products equal to the vinylidene fluoride-hexafluoropropylene copolymers, and plans for larger scale preparation of this new high temperature elastomer, designated as Fluorocarbon Elastomer 214, were made[55]. Unfortunately, adequate quantities of the hexafluoropropylene were not available, and considerable delay was encountered in attempts to prepare sufficient quantities of the elastomer for extensive compounding and evaluation studies.

During this interim period, the E. I. duPont de Nemours & Company[56,57] disclosed in September 1956 the development of a new fluorine-containing elastomer based on the vinylidene fluoride-hexafluoropropylene copolymer system. While the detailed history of this development is not disclosed, Rugg[56] points out that the research was stimulated by the demands for heat and fluid resistant elastomers resulting from advances in design in the aircraft and allied fields. This almost simultaneous disclosure of similar elastomers by two major industrial organizations may appear unusual, but there is little doubt that the present availability of "Fluorel"* and "Viton A"** is the result of both cooperative and competitive efforts to produce superior high temperature resistant elastomers based on fluorocarbon polymers.

During the time the fluorocarbon polymers were undergoing intensive investigation in attempts to prepare low temperature fluid resistant elastomers, research on fluorosilicone polymers was also being directed toward this same objective. Postelnek[58] erroneously stated at the 1958 Gordon Research Conference on Elastomers that investigation of fluorinated silicone rubbers was undertaken in the search for a high temperature elastomer. Actually, the Air Force sponsored research, initiated in July 1951 at the Purdue Research Foundation, had as its objective the synthesis of fluorine-containing silicone polymers which, if elastomeric, were to be evaluated as low temperature fuel resistant materials. While this original contractual effort did not result in useful elastomers, knowledge gained under the program[59] eventually led to the only polymer which approached fulfillment of the original objectives of Air Force and Army polymer research programs.

Early work by McBee and others[60,61] during the 1951 to 1954 period resulted in several methods for the preparation of fluoroalkyl silicone monomers through

* Reg. T. M., Minnesota Mining and Manufacturing Company.
** Reg. T. M., E. I. duPont de Nemours & Company.

reaction of fluoroalkyl organometallic reagents on alkoxysilanes. While elastomeric homopolymers could not be produced[62], several copolymers with a dimethyl silicone monomer yielded elastomers exhibiting considerable improvement in fuel resistance. Subsequent work by Tarrant, Dyckes and Wise[63] at Peninsular Chemresearch Inc. from 1954 through 1957 produced a number of fluoroalkysilane monomers at least one of which, trifluoropropyl methyldichlorosilane, was later polymerized to a heat and solvent resistant gum.

In an attempt to obtain useful elastomeric polymers from these available fluoroalkyl silicone monomers, a cooperative program between Wright Air Development Center and the Dow Corning Corporation was arranged on a noncontractural basis. This program ultimately resulted in the development and production of the product announced commercially in September 1956 as Silastic* LS-53. As described later, this elastomer exhibits a unique combination of high temperature stability, fluid resistance, and low temperature flexibility.

From this historical summary, it can be seen that the special purpose high temperature elastomers available in 1959 actually resulted from a search for low temperature, fluid resistant elastomers initiated in the early 1950's. Many industrial organizations, universities, and individual scientists not mentioned here made substantial contributions to these programs either on a subcontractual or personal basis. Their efforts are recorded in detail in the reports referenced.

V. PROPERTIES AND APPLICATIONS OF SPECIAL PURPOSE HIGH TEMPERATURE ELASTOMERS

The rapid advances being made in compounding techniques and ingredients for the special purpose high temperature polymers make it impractical to present extensive data on specific physical properties or on the effect of various environments on these properties. Therefore, the data following should only be considered examples of what can be accomplished with the present state of the art in elastomer compounding technology. In most cases, examples of the effect of long term heat or heat and fluid aging are presented along with more recent data on the effect of heat on properties *at* temperature. No attempt is made to provide a handbook on properties of high temperature elastomers, since in most cases such data would be obsolete before they were published. Where practical, significant deficiencies of the elastomers under discussion will be noted along with their outstanding properties.

A. ACRYLATES

The acrylic elastomers have not found extensive application in the aircraft industry, but due to increased temperatures in transmissions and to the introduction of sulfur containing oils and high pressure lubricants, are finding increased usage as seals and gaskets in the automotive industry[31]. In spite of low temperature deficiences which are unfavorable for aircraft applications, these elastomers were not ignored during the intensive effort previously mentioned to find suitable materials for contact with the diester engine lubricants. One of the better polyacrylate compounds developed by Mueller and others[19] at Battelle exhibited no cracking and excellent retention of original properties after 500 hours at 350° F as shown in Table VIII.

* Reg. T. M., Dow Corning Corporation.

TABLE VIII

PROPERTIES OF AN ETHYL ACRYLATE–CHLOROETHYLVINYL ETHER COPOLYMER COMPOUND

Hycar 4021	100
Triethylenetetramine	1.5
Stearic acid	1
Tetramethylthiuram disulfide	2
Silene EF	70

Cure 30 min @ 310° F
Postcure 7 hrs @ 350° F

Original properties	Press cure	Post-cure
Tensile strength, psi	1080	1260
Elongation, %	430	100
Hardness, Shore A	85	93
Aged in Turbo Oil-15* 500 hrs @ 350° F	**Press cure**	**Post-cure**
Tensile strength, psi	1000	1240
Elongation, %	100	90
Hardness, Shore A	64	72
Volume swell, %	43	36
Cracking	none	none

* Turbo Oil-15, a diester-type lubricant-product of Esso Standard Oil Company.

A similar compound withstood 500 hours aging at 400° F with no cracking, but exhibited excessive volume increase and loss in original properties. These results are significantly better than those obtained with NBR compounds, and only the timely availability of the fluoroacrylates prevented extensive engine application of the standard acrylic elastomers.

Similarly, the polyacrylates showed outstanding resistance to experimental hydraulic fluids for short periods at 550° F[64]. Application of compounds similar to that shown in Table IX was actually scheduled for advanced missile systems where such temperatures were anticipated.

Finally, under the work at Firestone previously discussed, curing systems were developed for poly (ethyl acrylate) based on metal oxides, ethylene glycol, and an amine which resulted in vulcanizates exhibiting tensile strengths as high as 690 psi *at* 500° F combined with good heat aging resistance at 400° F[65].

TABLE IX

PROPERTIES OF AN ETHYL ACRYLATE–ACRYLONITRILE-COMPOUND

Acrylon EA-5	100
Triethylenetetramine	2
Stearic acid	1.25
Tetrone A	2
HAF black	40

Unaged properties	
Tensile, psi	2000
Elongation, %	170
Hardness, Shore A	79
Aged in MLO 8200 3 hrs @ 550° F	
Tensile, psi	830
Elongation, %	200
Hardness, Shore A	63
Aged in MLO 8200 5 hrs @ 550° F	
Tensile, psi	320
Elongation, %	220
Hardness, Shore A	45

Since the polyacrylates appear to offer definite advantages in dynamic properties, strength at temperature, and cost over the fluorocarbon elastomers and the silicones, they should continue to receive serious consideration in high temperature applications.

B. SILICONES AND MODIFIED SILICONES

The silicones are without doubt the most versatile of the special purpose high temperature elastomers available today. From an unimpressive beginning in the early 1940's, at which time tensile strengths af 200–400 psi were the maximum obtainable, these materials have undergone such major improvements that some present elastomers are almost equivalent to general purpose rubbers in mechanical properties, with the added advantages of extremely low freezing temperatures (below minus 180° F), high temperature stability (above 600° F), and fuel and solvent resistance.

These advances resulted from polymer modifications, improved polymerization techniques, and intensive studies of reinforcing agents. While considerable study of vulcanizing agents has been made, benzoyl peroxide, first reported by General Electric[66] is still the most favored.

In addition to a wide range of properties obtainable from the various polymers and compounded stocks supplied by the three commercial producers—General Electric, Dow Corning and Union Carbide—a versatile group of end products ranging from molded, calendered, and extruded items through sealants, adhesives, and potting compounds can be prepared. Since full information on these materials may be obtained from the above mentioned suppliers' literature, only a few examples of significant properties of silicone elastomers are presented here.

One outstanding example of high temperature performance from a commercially available, general purpose silicone elastomer is noted in Dow Corning's Silastic 52[67]. After molding 5 minutes at 240° F and oven curing 24 hours at 480° F, this already formulated silicone base elastomer exhibits good retention of properties after 72 hours at 600° F.

	Original	72 hrs at 600° F
Tensile, psi	900	550
Elongation, %	270	60
Hardness, Shore A	52	75

Similar performance has been noted in materials of other suppliers, for example, compounds based on Union Carbide's XKW 1300. Such compounds have been under investigation for 600° F jet engine starter hoses.

While the commercial suppliers have made significant advances in the basic silicone polymers, several independent rubber fabricators have made valuable contributions to compounding technology with these polymers. One organization which has been continually active in this field and has been responsible for a number of important advances, under both Department of Defense contracts and their own research efforts, is the Connecticut Hard Rubber Company. Personnel of this organization were the first to report high strength (above 1200 psi) silicone compounds obtained from the use of surface treated silica. Also, they were the first to undertake extensive evaluation of the properties of silicone compounds *at* high temperatures[68], although similar studies were later carried out by Konkle and others[69] who compared properties *at* temperature of organic and silicone rubbers.

TABLE X

EFFECTS OF AGING SILICONE RUBBER COMPOUND

Test	Original 24 hrs @ 480° F	550° F 72 hrs	550° F 168 hrs	650° F 4 hrs	650° F 12 hrs	650° F 24 hrs	700° F 0.5 hr	700° F 1 hr	700° F 2 hrs
TS	1300	1050	950	1100	900	750	1050	750	550
E	350	260	230	330	280	200	350	300	270
H	55	55	60	55	58	60	45	45	50

Test	750° F 4 min	750° F 6 min	750° F 8 min	800° F 2 min	800° F 4 min	800° F 6 min
TS	1150	950	850	1100	700	200
E	370	370	380	350	350	200
H	50	48	44	52	45	40

H—Shore "A" Hardness

As a result of recent studies by Connecticut Hard Rubber, Grabicki[70] states as follows:

"Generally speaking, the life of silicone rubber shows an exponential relationship to the temperature of aging. The life is almost indefinite at about 400° F, decreases to weeks at 550° F, days at 650° F, hours at 700° F, minutes at 750° and 800° F, and seconds at 1000° F. Above this temperature, the major problem is combustion in the presence of oxygen or reversion in the absence of oxygen".

This concise statement of the useful life of silicone rubbers at high temperatures is an excellent summary of the current state of the art in development of high temperature elastomers of any type. That is, other than the silicones, no

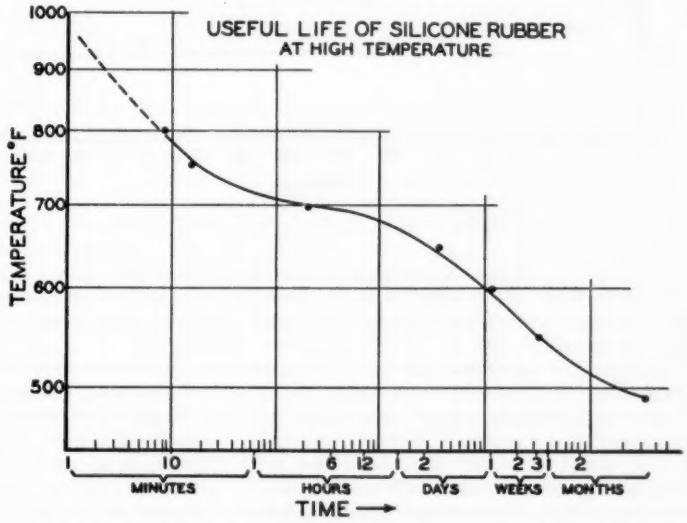


FIG. 5.—Useful life of silicone rubber at high temperature. From Reference 70.

elastomeric materials are available at this writing which exhibit aging properties equal to those obtained to support the above quotation and presented in Table X. These results are also presented graphically in Figure 5 to further illustrate the high temperature behavior of available silicone elastomers.

A serious deficiency in silicone elastomers is the tendency to revert at extremely high temperatures, a tendency that is markedly accelerated when the rubber is confined or in vacuum. Wide variance in reversion resistance is found among compounds using different silicone gums, fillers, and curing agents. Water, which is absorbed in many common mineral reinforcing fillers, is quite deleterious to high temperature aging properties, and the use of a fumed silica or other "dry" filler is essential for extreme high temperature stability. Bobear[71], in a study of aging silicone rubbers in sealed systems, reports that considerable degradation occurs merely from conditioning fully cured stocks for one week at 80° F, 60 per cent to 100 per cent relative humidity, then aging 24

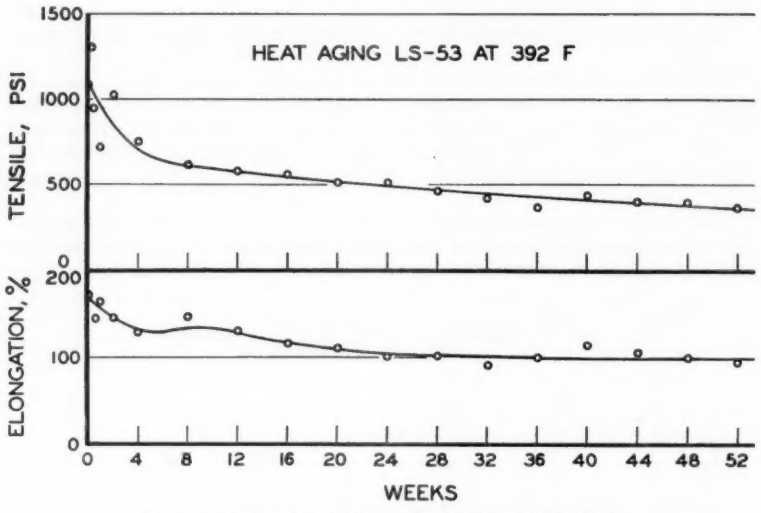


FIG. 6.—Effect of prolonged heat aging at 392° F on Silastic LS-53.

hours at 480° F. Bobear found that use of vinyl-containing silicone gums, fumed silica fillers, di-*tert*-butyl peroxide curing agent, and proper postcure, along with care in processing to avoid moisture, enhances aging resistance of confined products.

In general, the solvent resistant silicone elastomers exhibit the same mechanical properties, low and high temperature behavior, and processing characteristics as the conventional polysiloxane elastomers. While the three manufacturers previously mentioned each market a solvent resistant silicone elastomer, only two distinct types are available. They are the fluorosilicone elastomers, and the nitrile silicone or cyanosilicone elastomers. An almost infinite number of copolymer compositions are available from which to produce the latter family of elastomers, but all are based on introduction of a C≡N group at some posi-

tion on an alkyl side chain of the polysiloxane. Williams, Pike and Fekete[72] state that the cyanoalkyl silicone elastimers constitute a large group of rubber-like materials which possess solvent resistance over a wide temperature interval. While there is little doubt that this family of elastomers does exhibit fuel, oil, and solvent resistance far superior to the conventional silicones, data on presently available polymers indicate that the fluorosilicones are even more superior in the combination of high temperature stability and solvent resistance. This superiority may only be important in critical aircraft fluid systems where a broad range of environments are encountered, and may be relatively unimportant in many industrial applications where environments are less severe and a cost advantage of the nitrile- or cyanosilicones may make them attractive.

However, until definite improvements have been made in this latter family of elastomers, the fluorosilicones, as represented by Silastic LS-53 or LS-63, must be considered as superior in those applications requiring the maximum in heat stability and fluid resistance. Heat stability of the fluorosilicones is demonstrated in recent unreported data[73] supplied by the Dow Corning Corporation and presented in Figure 6.

TABLE XI

VOLUME SWELL OF A FLUORINATED SILICONE RUBBER, SILASTIC LS-53, IN VARIOUS FLUIDS

Fluid	Time, 3 days Temperature	Volume swell, %
Jet fuel (JP-4) Military Specification MIL-F-5624	350° F	+23
ASTM No. 3 oil	300° F	+ 4
Diester base jet engine oil Military Specification MIL-L-7808	350° F	+ 9
High temperature aircraft hydraulic fluid (Oronite 8515) Military Specification MIL-H-8446A	400° F	+14
Petroleum base hydraulic fluid Military Specification MIL-H-5606	200° F	+ 6
Lubricating oil, SAE 10	300° F	+ 2

Talcott, Brown and Holbrook[74] describe the swelling behavior of the fluorosilicones and demonstrate the excellent resistance to aircraft and industrial fuels and lubricants as shown in Table XI.

While these data indicate the desirable properties of the fluorosilicones, it must be pointed out a *combination* of heat stability and fluid resistance can not always be obtained, particularly in the aromatic fuels. Swelling in such fuels at high temperatures and subsequent loss of physical properties is considered excessive, and tends to limit the usefulness of these elastomers to a temperature of approximately 350° F as shown in Table XII[75].

This table is merely intended as an example of the behavior of a specific elastomer under the combined environment of heat and fluid, but it clearly indicates the necessity for investigating any new elastomer under conditions approaching as closely as possible those to be encountered in actual service. Some manufacturers make claims of high temperature resistance and fluid resistance but verification of "high temperature fluid resistance" is always necessary. Similarly, claims of fuel resistance must be carefully investigated since numerous instances of manufacturers' literature showing change in volume or physical properties in "jet fuel" have been observed. Misleading data, which tend to make a product look better than it actually is, may be obtained

by immersion in commercial jet fuels containing no aromatics. However, both military and commercial aviation fuels may vary from 0 to 25 per cent in aromatic content, and recent automotive fuels vary even more widely. Since, in general, the aromatic content of the fuel determines extent of deterioration of most conventional and special purpose elastomers, it is important that data be obtained in 70:30 isooctane-toluene blends, as represented by ASTM Reference Fuel B, in order to obtain a realistic indication of fuel resistance.

As has been shown, advances in the entire field of silicone elastomers have been almost spectacular during the past 5–10 years. Important mechanical properties such as tensile strength and tear resistance have been doubled; swell in petroleum base fluids has been reduced from above 200 per cent to less than 20 per cent; temperature range of serviceability has been broadened to from below minus 180° F to above plus 600° F; and, according to Warrick[76], polymer modifications have provided elastomers with greatly increased resistance to nuclear radiations. Evidence at the present time indicates that even further

TABLE XII

AGING DATA ON SILASTIC LS–53 IN ASTM REFERENCE FUEL B

	Original properties	Aged in ASTM Reference Fuel "B" (70/30 isooctane/toluene)		
		70 hrs @ 73° F	70 hrs @ 275° F	70 hrs @ 400° F
Tensile strength, psi	1000	750	625	275
Elongation, %	180	180	150	200
100% modulus, psi	525	500	360	80
Hardness, Shore A	59	55	45	15
Volume swell, %	—	20	30	40

improvements in all properties are possible and will result from polymer and compounding research now under way.

C. FLUOROCARBONS

Fluoroacrylate polymers.—The fluoroacrylates of interest include poly 1,1-dihydroperfluorobutyl acrylate (Poly-FBA or 3M Brand Fluoro-Rubber 1F4) and perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate (Fluoro-Rubber 2F4). This family of polymers actually represented the first practical flourine-containing elastomeric materials developed, and their vulcanizates exhibited a balance of physical properties, including high-temperature fuel and oil resistance, never before obtained in a rubberlike material. While original properties were not outstanding, aging at high temperature resulted in better retained properties than could be obtained with the NBR elastomers.

At the conclusion of three years of intensive effort on the compounding and evaluation of Poly-FBA at the Materials Laboratory, Wright Air Development Center, Hamlin stated[46]:

"A large number of fluorine-containing polymeric systems have been investigated by the Minnesota Mining and Manufacturing Company under Air Force Contract No. 33(038)–515. One of the most successful developments, Poly 1,1-dihydroperfluorobutyl acrylate (Poly-FBA) exhibits good rubbery characteristics, excellent resistance to many fuels, lubricants, solvents, chemcals, and ozone, plus very good stability at elevated temperatures. Com-

pounding and processing studies have been made, and tests conducted in various media at temperatures up to 550° F. Results of laboratory and simulated service tests show Poly-FBA to be vulcanizable through the action of certain metal oxides or organic amines, reinforcible with carbon blacks and some inorganic fillers, and readily handled on standard rubber processing equipment. Tensile strength ranges from 1000 to 1400 pounds and elongation from 200 to 400 per cent. It is highly resistant to the effects of hydrocarbon fuels, even at elevated temperatures, and has been successfully tested in the presence of synthetic lubricants for up to 300 hours at 400° F, and for shorter periods at higher temperatures.

"Poly-FBA is also highly resistant to the chemical action of fuming nitric acid, although quite permeable to it. It is completely resistant to ozone. Low temperature properties are limited to about 0° F unplasticized, although it retains good elasticity almost down to the brittle point".

The superiority of Poly-FBA elastomers over NBR compounds is clearly demonstrated in Hamlin's data on a typical Poly-FBA recipe shown in Table XIII.

TABLE XIII

PROPERTIES OF A POLY FLUOROBUTYLACRYLATE COMPOUND

Poly FBA	100
Triethylenetetramine	1.25
Sulfur	1
Stearic acid	1
SAF black	35

Cure 60 min @ 310° F

	Original properties	Aged in Diester Based Jet Engine Oil (MIL-L-7808) in open test tubes		
		250 hrs @ 350° F	500 hrs @ 350° F	1000 hrs @ 350° F
Tensile strength, psi	1300	1080	1020	870
Elongation, %	390	220	250	300
100% modulus, psi	350	630	540	470
Set at break, %	32	13	18	42
Hardness, Shore A	63	74	75	70

However, as previously indicated, the subsequent development of superior special purpose high temperature elastomers has resulted in a rapid decline in the relative usefulness of the fluoroacrylates, and, unless some unique combination of environments is encountered, future prospects for increased usage of these elastomers are not considered promising.

Fluoropolyesters.—In 1954 research on condensation type elastomers was initiated at the Hooker Electrochemical Company under Air Force sponsorship. The objective of this program was development of an elastomer exhibiting thermal stability (350° F or higher), fluid resistance, and flexibility at minus 65° F or lower. Early in the program, Schweiker and coworkers[77] found that hexafluoropentylene adipate, prepared from a reaction of adipyl chloride and 2,2,3,3,4,4-hexafluoropentanediol, could be crosslinked to a tough elastomeric material. Further studies[78] with this fluoropolyester indicated that with proper reinforcement and crosslinking, useful elastomers exhibiting good mechanical properties, resistance to heat aging in air and fluids at 350–400° F, and a brittle temperature of minus 98° F could be obtained. Unfortunately, crystallization

of the elastomer at moderately low temperatures seriously limited its usefulness, and all attempts to overcome this deficiency through preparation of other polyesters and copolyesters were only partially successful. Subsequent development of the fluorosilicones and other improved special purpose elastomers resulted in declining interest in the fluoropolyesters.

Chlorotrifluoroethylene-vinylidene fluoride copolymers.—At the time of their development, these copolymers, better known as the Kel-F Elastomers, exhibited resistance to dry heat aging which was surpassed by only silicone base materials. Also, Smith and coworkers[22] found that one grade of Kel-F Elastomer when properly compounded exhibited a useful retention of physical properties after 500 hours at 400° F in JP-5 (sample contained 14.8 per cent aromatics) and in ASTM Reference Fuel B (70:30 isooctane-toluene). The formulation and aging data shown in Table XIV represent results of an intensive investigation of elastomers for high temperature fuel service.

While the Kel-F elastomers have received considerable study[50,79,80] for high temperature application as seals, hose, diaphragms, tanks, and others, certain

TABLE XIV

PROPERTIES OF A KEL-F 3700 COMPOUND

Kel-F 3700	100
HMDA carbamate	4.5
Zinc oxide	10
Dyphos	10

Cure 30 min @ 350° F
Postcure 16 hrs @ 350° F

Original properties		Properties after aging 500 hrs @ 400° F	
		Jet Fuel (JP-5)	ASTM Reference Fuel B
Tensile strength, psi	3050	560	580
Elongation, %	330	460	300
Hardness, Shore A	62	49	38
Volume swell, %	—	+25	+47
180° Bend test	—	Pass	Pass

property deficiencies have been noted. Principal disadvantages which have tended to limit usefulness include fabrication difficulties in producing finished items such as "O"-ring and other seals, and relatively poor resistance to compression set at elevated temperatures, a serious problem in seal and gasket applications. For such reasons the vinylidene fluoride-hexafluoropropylene copolymers may be expected to replace the Kel-F elastomers in many current and future applications.

Vinylidene fluoride-hexafluoropropylene copolymers.—This family of copolymers, which have been, or currently are better known under the designations of Fluorocarbon Elastomer 214, "Fluorel", "Viton" A, and "Viton" A-HV, represents one of the most important single advances in special purpose high temperature elastomers in recent years. Wilson, Griffis and Montermoso[81,82] compared Fluorocarbon Elastomer 214 and Kel-F Elastomer 3700 in heat and chemical resistance and found the former to be superior after high temperature exposure in air, diester engine oils, synthetic hydraulic fluids, and 70:30 isooctane-toluene test fluid. Griffin[83] confirmed these findings after studying "Viton" A compounds in a variety of high temperature fluid envir-

onments, and he further stated that "Viton" A showed good possibilities for service over the temperature range of minus 65° F to plus 600° F.

Such data clearly indicate that these fluorocarbon copolymers, when properly compounded, provide elastomers exhibiting a combination of heat and

TABLE XV

PROPERTIES OF A VINYLIDENE FLUORIDE–HEXAFLUORO PROPYLENE COMPOUND DESIGNED FOR HIGH TEMPERATURE SERVICE

Formulation:

VITON A	100	Press cure: 30 min/300° F
MT black (Thermax)	25	Followed by: 1 hr/212° F
Maglite K*	20	250° F, 300° F, 350° F, and
HMDA carbamate**	1.3	24 hrs/400° F in oven

Original properties	Obtained			MIL-R-25897A Specification requirements
Tensile strength, psi	2220			1800 min
Elongation, %	220			175 min
Hardness, Shore A-2	73			70±5
	After 70 hrs/250° F, 25% deflection			
Compression Set, %***	23.6			25 max.
	After air aging, 16 hrs/600° F			
	Original	Aged	Change or % change	
Tensile strength, psi	2260	1610	−29%	−35 max.
Elongation, %	260	180	−31%	−50 max.
Hardness, Shore A-2	73	84	+11	+15 max.
Weight loss, %			5.7	10 max.
	After 72 hrs/400° F, in MLO 8200			
Tensile strength, psi	2290	1920	−16%	−20 max.
Elongation, %	260	195	−25%	−25 max.
Hardness, Shore A-2	73	72	− 1	± 5
Volume change, %			4.2	1 to 10
	**** After 72 hrs/400° F in di-2-ethylhexyl sebacate with 1/2% phenothiazine			
Tensile strength, psi	2320	1780	−23%	−25 max.
Elongation, %	260	260	0	−10
Hardness, Shore A-2	73	65	− 8	±10
Volume change, %			13.9	1 to 15
	After 72 hrs/R. T. in MIL-S-3136 type III fuel (ASTM Ref. Fuel B)			
Tensile strength, psi	2340	2240	− 4%	−10 max.
Elongation, %	260	260	0	−10
Hardness, Shore A-2	73	72	− 1	± 5
Volume change, %			2.4	0 to 5

* T. M. of Merck & Co., Inc.
** du Pont's DIAK No. 1 was used.
*** Specimens made by plying up five 0.5 in. diam. × 0.1 in. thick specimens.
**** Used Anderol 774 supplied by Lehigh Chemical Co., Chestertown, Maryland.
Tensile tests were on standard ASTM dumbbells, 0.075 in. thick. Split sheet method used for aging and immersions.

fluid resistance not obtainable from any other currently available rubberlike material. Further, as with many other new developments, continued improvement in properties has been obtained through polymer modifications and compounding studies.

Early investigations of both Fluorocarbon Elastomer 214[81,82] and "Viton"

A[57] were conducted on peroxide cured vulcanizates. However, it was later found[84] that a better balance of physical properties, including tensile strength, heat resistance, and compression set resistance, could be obtained from compounds cured with hexamethylenediamine carbamate (HMDA-carbamate), and this agent receives the most attention at the present time.

Unfortunately, other than manufacturers' literature, few references have been made available to date on the compounding and properties of the vinylidene fluoride-hexafluoropropylene copolymers. Moran and Eubank[85] point out that "Viton" A and A-HV can be cured by polyfunctional amines, peroxides, and high energy radiation and that both black and mineral fillers may be employed for improvement of specific properties. They also show the value

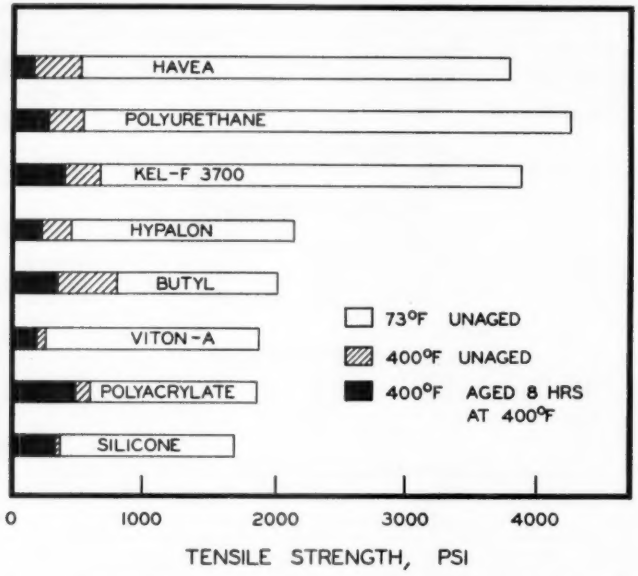


FIG. 7.—Tensile properties of vulcanizates *at* 73° and 400° F before and after heat aging eight hours at the test temperature. From Reference 13.

of acid acceptors such as magnesium and lead oxide in obtaining a high state of cure and maximum heat resistance, The importance of the type or grade of magnesium oxide used in obtaining maximum heat resistance was first noted by Griffin[86] during studies in which he compared commercial light calcined magnesia with C. P. grade magnesium oxide. His findings that the latter grade provided greatly superior heat resistance were further investigated by chemists of Merck and Company, Marine Magnesium Division, who compared their various commercial and experimental grades of Maglite* in a typical "Viton" compound[87]. Their results confirmed that for maximum resistance to compression set and retention of properties at high temperatures, one grade, Maglite K, was definitely superior to the others which they produced. Their at-

* Reg. T. M., Merck and Company.

tempts to meet the very stringent requirements of a current Military Specification, MIL-R-25897A[88], resulted in a superior formulation for vinylidene fluoride-hexafluoropropylene copolymer compounds. The properties which may be expected from such a formulation are shown in Table XV.

In this specification, which was designed to provide compounds with maximum heat stability, the 600° F air aging test and the compression set requirements are the most critical, However, a number of industrial fabricators have successfully qualified, and are producing high quality finished products. These products which include "O"-ring seals, fuel tanks, hose, and other items are currently undergoing tests or are already in use in aircraft and missile applications under extreme environments.

Techniques for preparing room temperature vulcanizing compounds have been reported[89], and only the unavailability of a liquid copolymer has prevented intensive investigation of this family of copolymers for such applications as sealants, caulking and potting compounds, and other uses where high temperature fluid resistance is essential.

Deficiencies of these elastomers include high cost, marginal low temperature properties for a number of applications, and significant loss in physical properties *at* elevated temperatures. This latter deficiency, however, is common to all currently available special purpose high temperature elastomers as shown in Figure 7. Attempts to overcome this loss in strength in elastomers as temperature is increased still represents one of the major challenges to polymer chemists and elastomer technologists.

VI. ADVANCED RESEARCH ON HIGH TEMPERATURE POLYMERS

It can readily be shown that elastomer research during the past ten years has produced advances equally as significant and impressive as those in the fields of metallurgy, plastics, ceramics, and other materials of construction. Combinations of materials properties which were considered almost impossible to obtain by the rubber industry only 5–10 years ago are now provided by the fluorocarbon polymers and the silicones.

Since any significant extension of the high temperature capability of these elastomers is considered unlikely, research must be directed into other new and previously unexplored areas of chemistry in attempts to uncover leads to a major breakthrough in the area of high polymers. While research of this type is being pursued by many industrial organizations, much of it remains unreported. However, in attempts to stimulate new ideas, such research conducted or sponsored by Department of Defense Laboratories is quite freely discussed in the scientific community, and technical reports are made available to interested and qualified scientists. A brief discussion of the direction of the work currently under way is, therefore, considered pertinent to this review.

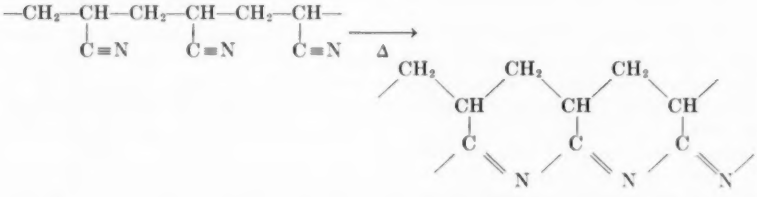
The research on polymers includes mostly work on hitherto little-explored but possible routes to new polymeric materials and studies in the general areas of both organic and inorganic chemistry. In addition to and significantly affecting the direction of the synthetic work are studies on the experimental and theoretical aspects of thermal stability. These studies, as might be expected, are quite complex, and considerable effort is still necessary to more fully define this very important area. The synthetic work at this time is primarily exploratory and designed to furnish quite basic information regarding the chemistry of representative organic and inorganic compounds.

Research in this area of new polymers is not limited to a search for new high

temperature elastomers but is continued in support of all applications requiring high temperature polymers. It would be extremely difficult to predict the nature or physical properties of many of the new polymers expected from advanced research. Therefore, it would not be possible to stipulate that a particular program should produce only elastomers, or only transparent plastics, or only fluids and so on. Admittedly, the synthesis of polymers having useful rubbery properties is probably more difficult than the synthesis of polymers for other applications.

One of the preliminary steps made toward the preparation of thermally stable polymers was a search through existing materials in an effort to deduce empirical relationships between structure and thermal stability. A considerable amount of information has resulted. Much of this information has found use in the preparation of thermally stable low polymers—fluids for aircraft and other applications. Many aromatic compounds display a high thermal stability. Benzene, for example, has been reported to be stable at 1000° F[90]. Polyphenyl fluids[91] have been synthesized as well as polyphenylethers[92], both of which show good thermal characteristics[93,90]. Further extension of these materials into high-molecular weight polymers has yet to be achieved, and little chance is seen for producing elastomers until some means can be found to impart sufficient flexibility and length to these polymer chains.

Another method for increasing the thermal stability of organic polymers might result from operations on already formed polymers. For example, partially degraded polyacrylonitrile is believed to contain such a microstructure as represented below:



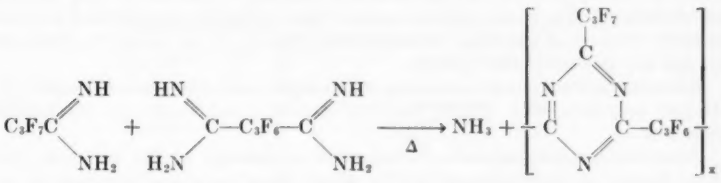
Such a structure should contribute materially to enhanced thermal stability. The application of such structural features to other organic polymers may well be feasible and could result in useful polymeric materials.

A number of coordination compounds have been found to possess considerable thermal stability[94], suggesting possible thermally resistant polymers using the principles of coordination chemistry. Fernelius at the University of Pennsylvania[95] and Bailar at the University of Illinois[96] have investigated possibilities in this area. Results indicate that many chelates are stable as low polymers, but the difficulty in preparing high-molecular weight coordination compounds has prevented any significant success in this area to date.

In the inorganic field, an extremely large number of compounds exist that have excellent thermal stability. While inorganic high polymers have been prepared, frequently in forms such as brittle glasses, very little work has been done on the synthesis of useful polymers. To use the potential of thermal stability existing in inorganic compounds, knowledge of polymer chemistry in this area must be brought to a level more nearly approaching that of organic polymer chemistry.

In the interim, however, exploratory polymer research continues in a number of areas. Several pertinent examples of programs now under way follow:

Polyamidines.—One of the most interesting polymers investigated recently is the product of the pyrolytic condensation of a perfluoro-monoamidine and a perfluorodiamidine as represented by the following reaction:



Brown at the University of Florida, under a research program supported jointly by the Office of Naval Research and Wright Air Development Center, first prepared these polymers[97]. Their physical characteristics range, depending on conditions, from brittle resins to elastomeric solids. The elastomer, particularly, evoked considerable interest due to its good thermal stability upon heating in air, and resistance to strong, oxidizing mineral acids. The elastomeric gum can be heated in air at over 570° F for long periods of time with no apparent decomposition. After heating in air at much higher temperatures (840° F), the polymer loses weight (up to 50 per cent in ½ hour) but retains a high degree of its rubbery character[58].

The primary deficiency of the polymer lies in the fact that it is highly crosslinked, thus rendering it unsuitable for most applications. The polymer structure given in the above reaction, therefore, must be considerably idealized. Infrared studies on the polymer indicate that the basis structural unit is the *s*-triazine unit as shown, but a significant number of these triazine nuclei apparently must be tri-substituted, producing insolubility.

In addition to the pyrolytic reaction shown above, polymerization may also be effected by melt and solution reactions employing free-radical and ionic initiators[98]. However, these products also are crosslinked. Further investigations are under way in an effort to produce linear, high polymers.

Phosphorus-nitrogen polymers.—Phosphonitrilic dichloride, $(NPCl_2)_x$, has been known for some years. This polymer displays rubbery properties, but suffers considerably from hydrolysis in air. The fact that rubbers can be produced from the phosphorus-nitrogen system, however, has prompted many investigators to consider derivatives of this polymer with hopes of reducing its hydrolytic susceptibility. Following usual methods of preparation, the phosphonitrilic dichlorides exist in a variety of forms—low molecular weight ring compounds, primarily trimeric and tetrameric, and up to moderate length linear polymers. Most methods of preparing derivatives involve the reaction of these low molecular weight ring compounds with suitable reagents. Methyl[99] and phenyl[100] substituted phosphonitrilics have been reported. However, these materials were found not to polymerize well, if at all. The fluoride[101,98] and bromide[102] analogues have been synthesized, but apparently offer little advantage over the parent phosphonitrilic dichloride with regard to hydrolytic tendencies.

Recently, Audrieth[103] of the University of Illinois has announced the preparation of the trimeric and tetrameric phosphonitrilic di-isothiocyanates. Polymers have been prepared from these species either by heating alone in air or vacuum, or by the addition of materials capable of reacting with the isothiocyanate groups, e.g., diols, diamines, etc. The thermally polymerized polymers

were found to be quite highly crosslinked, rather soft resilient materials, slowly attacked by moist air. In addition the polymer lost weight significantly at temperatures greater than 390° F. The structure of this polymer has not been definitely established, but polymerization is believed to proceed by ring opening and extension. The highly gelled nature of the thermally polymerized polymer indicates that some reaction, perhaps with impurities or moisture, proceeds through the isothiocyanate groups.

Research in this area is continuing in attempts to produce linear phosphorus-nitrogen polymers with higher thermal stability and improved mechanical properties.

Aluminum-oxygen polymers.—Somewhat in analogy to the silicones, polymers having an aluminum-oxygen backbone have been, and continue to be, a subject of investigation. The high bond-strength of the aluminum-oxygen bond (120–136 kcal/mole)[104] as compared with the silicon-oxygen bond in the polysiloxanes (101 kcal/mole)[105] and the carbon-carbon bond in ethane (86 kcal/mole)[106] would appear to make this system attractive from a stability standpoint (presuming that oxidative and hydrolytic reactions can be avoided). However, the attendant rise in per cent ionic character[107] of the bonds going from carbon-carbon (ethane, 0 per cent), silicon-oxygen (polysiloxanes, 51 per cent) to the aluminum-oxygen (triisopropoxy aluminum, 63 per cent), may indicate that the chances of producing elastomeric aluminum-oxygen polymers will be difficult due to relatively high inter-chain attraction.

Considerable work, both in this country and abroad, has been done in efforts to prepare aluminoxanes. Some of the synthetic routes employed are shown below:

(1) Hydrolysis:

(a)[98] $ROAL(R'_2) \xrightarrow{H_2O} \left[\begin{matrix} Al{-}O \\ | \\ R \end{matrix} \right]_x$

(b)[98] $ROAl(OR')_2 \xrightarrow{H_2O} \left[\begin{matrix} Al{-}O \\ | \\ OR \end{matrix} \right]_x$

(c)[108–112] $Al[OSi(C_2H_5)_2]_3 \xrightarrow{H_2O} \left[\begin{matrix} Al{-}O \\ | \\ OSi(C_2H_5)_3 \end{matrix} \right]_x$

(2) Pyrolysis[98]

$$CH_3COO{-}\underset{\displaystyle OC_6H_5}{\overset{|}{Al}}{-}OC_3H_7 \xrightarrow[\Delta]{} \left[\begin{matrix} Al{-}O \\ | \\ OC_6H_5 \end{matrix} \right]_x$$

(3) Heterofunctional Condensation[98, 113]

$$RCOO\,Al(OH)_2 + (R'O)_2Al\,OOCR'' \longrightarrow \left[\begin{matrix} Al{-}O{-}Al{-}O \\ | \quad\quad | \\ OOCR \quad OOCR'' \end{matrix} \right]_x$$

Mainly, these methods have been characterized, thus far, by the formation of low and/or crosslinked polymers. It has been reported that Andrianov and coworkers[108–112] in the U.S.S.R. have met with some success in the polymerization of tris(triethylsilanoxy) aluminum by hydrolysis (Reaction 1(a) above). The polymers usually appear as insoluble, rather intractable materials showing

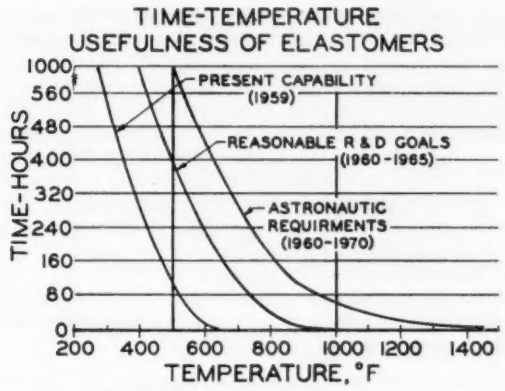
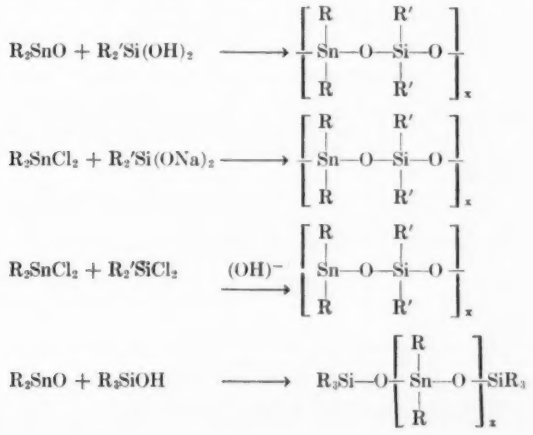


FIG. 8.—Present and predicted time-temperature capability of elastomeric materials.

no evidence at this time of rubberlike behavior. The thermal stability of the aluminoxanes depends to a large extent on the group attached to the aluminum atom. Particular attention has been devoted to those substituents which resist the catalytic activity of the electronically deficient aluminum atom. Such substituents as those containing nitrogen and oxygen, capable of donating electrons if necessary, appear to give the most thermally stable structures[98]. Introduction of the large bulky groups such as the triethylsilanoxy group into the polymer seems to aid somewhat in the hydrolytic resistance of the materials. However, such a large group which might be expected to allow less of an ordered structure in the polymer apparently does not increase significantly the flexibility or rubberlike properties of the polyaluminoxanes. Thus, elastomeric aluminumoxanes appear at present to be rather problematical.

Stannosiloxanes.—Such polymers have been prepared of relatively low molecular weight (1000 to 5000) using methods as given below[98,114]:



A variety of copolymers were prepared having Sn:Si ratios from 1:1 to 1:10. The polymers with the higher silicon content were found to be more thermally, oxidatively, and hydrolytically stable[98]. However, the order of thermal stability found was comparable to that of polydiphenyl siloxane.

As has been previously indicated, these systems and many others are being explored in an attempt to find leads to new thermally stable polymeric materials for a variety of applications. While the potential for producing useful elastomers from the systems now under investigation may not appear great, continued efforts must be maintained to meet the requirements of the forthcoming space age for such materials. Kelble[115] presents an interesting summary of the current state of the art, and anticipated future high temperature requirements, for elastomeric material as shown in Figure 8.

Failure to provide significant advances in high temperature elastomer technology could have serious effects in terms of performance and reliability of advanced air and space vehicles.

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NATURAL LATEX AS A COLLOIDAL SYSTEM

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I. INTRODUCTION

Natural rubber latex as a raw material for industry is relatively young. Although solid rubber has been known ever since the days Christopher Columbus and his men marvelled at the natives of Haiti playing with a ball made from the gum of a tree—which was in 1496—latex received little attention until the third decade of the twentieth century. By that time the rubber plantation industry had developed to such an extent that it appeared feasible to collect, preserve and transport latex on a large scale. Malaya was the first to export latex in commercial quantities in 1922, followed by Indonesia in 1926 and by Liberia in 1935.

At the outbreak of World War II annual world production of latex had reached 44,000 tons but it was not until 1948 that production was back at the same level again. The last ten years have shown a rapid increase with world production reaching 168,000 tons in 1957. This would not have been possible without the application to manufacturing of scientific methods which in turn were based on an ever increasing amount of fundamental knowledge of its properties.

It is well known that natural latex, as a liquid of biotic origin, may at times show considerable variations in composition and colloidal structure as the result of biotic, geotic, cilmatic and other influences. It is these differences which account for the variability in the properties of latex and rubber, a variability which is sometimes the cause of difficulties in processing these materials to a product of well defined and uniform properties.

Great strides have been made over the last twenty years and it is the purpose of this review to outline the principal facts regarding natural latex as a colloidal system and to indicate the progress made in this field of research.

I. MORPHOLOGY OF THE RUBBER PARTICLE AND MOLECULAR WEIGHT OF THE RUBBER HYDROCARBON

Natural rubber latex is a hydrosol, strongly protected by proteins, in which the rubber particles occur as aggregates of the molecules. As in all colloidal

substances, the shape and size of these particles are fundamental values and if they occur, as is generally the case in natural colloids, in a great variety of sizes, particle size distribution is another fundamental factor.

Preceding investigations[1] established that the size of latex particles varies from a diameter of 0.5 micron or less to 3 microns in adult Hevea trees. It was also found that a very large number of the particles were less than 0.5 micron in diameter and visible only with an ultramicroscope. Although early observers insisted that the particles of Hevea latex were spherical in shape, Hauser[2] has shown that a large number of them, especially in older trees, are oval or pear-shaped, or even have tails. The shape of the particles produced by a given tree seems to be peculiar to it, though very young trees generally produce only small spherical particles. Accepting the observation of non-spherical particles as correct, it then becomes necessary to determine whether these particles are originally present in latex as such or as combinations of smaller spherical units or whether they are formed under the conditions of microscopic manipulation techniques. Hauser was of the opinion that the egg- or pear-shaped particles in fresh Hevea latex were not the result of aggregation of small spherical particles. This conclusion was reached through microscopic studies with transmitted light after the particles had been embedded in a gelatinous dye which prevents aggregation[3]. This finding was also confirmed by the use of an ultramicroscope. On the basis of his studies by means of the ultraviolet microscope Lucas[4] came to the conclusion that the particles of Hevea latex are predominantly small shperes with a few larger pear-shaped or elongated particles and that some of the larger particles are formed by two or more small particles having joined but not merged.

Mathematical analysis of particle-size data indicated that only about 10 per cent of the particles in the latexes studied were larger than 0.50 micron. The diameter of the average particle was computed as 0.26 micron with a maximum of 2.0 microns and a minimum of 0.09 micron. McGavack[5] reported on the particle size distribution of latexes, modified by creaming or centrifuging whereby all particle sizes are eliminated which cannot be photographed with microscopical equipment in visible light. In this type of concentrate particle sizes ranged from 0.48 to 2.19 microns[7]. It was also concluded that the protein content of the particles is proportional to the surface area.

With the electron microscope it has been possible to obtain a useful magnification of 20,000 diameters. This has made it a most useful tool for investigations into the particle size region below the resolution of the light and ultraviolet microscopes. Rubber latexes have received some attention in this respect, although here the investigation is rendered difficult as the latexes must be dried out before insertion into the vacuum chamber of the microscope[6]. This technique was employed by Hendricks, Wildman and McMurdie[7] in their work on a large variety of latexes. The smallest natural rubber latex particles obersved had a diameter of about 0.03 micron. Morphological features were in general similar to those described by Lucas[4]. Pear-shaped particles were also apparent and appeared to be formed by coalescence of small spheres.

Observations of these early investigators seem to indicate that latex particles in many plants have form-retaining as well as fluid properties. The latter were demonstrated by Freundlich and Hauser[2] on a microscopic scale by micromanipulation. They postulate that the latex particle can be divided into three parts: first, the exterior, consisting of an adsorbed layer which is probably protein; beneath this, a skin of solid or gel rubber and within this skin a body of very viscous liquid rubber. Kemp[8] modified this concept by suggesting that

the outer film consists of a transitory layer of soap or lipide followed by an intermediate protein film and an inner skin of gel rubber. The fluid interior of the particle was postulated to be an emulsion of sol rubber containing sterol bodies. According to Hendricks and coworkers[7], properties of latex particles are equally in harmony with a simpler picture according to which the molecules are intertwined as if they were odd lengths of string packed into a loose ball with other latex constituents held between the meshes. However, later investigations have established the concept of a entwined mass of rubber molecules covered with an adsorbed layer of material of which soap like substances and proteins form the main constituents.

For the purpose of determining the weight-distribution curve of the rubber particles according to their diameter, Hessels[9–10] employed two methods, namely photomicrographic dispersoidal analysis and sedimentation analysis. The precision of the first method did not prove to be high but the sedimentation analysis was found to be very suitable for the purpose. By an accurate regulation of the viscosity, specific gravity and temperature of the suspension it became possible to determine the weight-distribution curve of latex to a diameter of about 0.4 micron within a creaming time of 10 to 14 days, while the total percentage of still smaller particles was also determined.

TABLE I

COMPOSITION OF PURIFIED RUBBER FROM DIFFERENT FRACTIONS HESSELS[8]

	Fract. 1	Fract. 3	Fract. 6	Fract. 8+9	Original
Nitrogen	0.04	0.07	0.07	0.11	0.10
Ash	0.05	0.16	0.20	0.52	0.15
Aqueous extract	0.5	1.0	1.2	1.7	0.6
Acetone extract	1.5	2.1	3.9	4.3	1.7
Fatty acids	0.7	1.2	2.4	2.7	0.7
Total non-rubbers	2.3	3.7	5.7	7.2	3.3

The basis of studies on the relation between particle size and composition of the latex is the fact that the nonrubber components present can be in solution (true or colloidal) in the serum or can be adsorbed reversibly or irreversibly on the surface of the rubber particles or possibly in the interior of the rubber particles. When latex is washed thoroughly the only non-rubber substances which remain are those that are adsorbed irreversibly. In this case there is a simple relation between the size of the particles and the composition of the rubber, viz., the percentage of adsorbed substances is proportional to the total surface of the particles, at least under conditions where the thickness of the adsorbed layer is uniform. Since the total surface per unit weight is inversely proportional to the diameter of the particles, the smaller the latex particles, the higher must be the proportion of non-rubber substances on the rubber. After having purified nine different fractions by dialysis and double precipitation Hessels[8] determined the total content of dry substances in each as summarized in Table I.

The relation between particle size and substances dissolved in the serum was studied by comparing, for each fraction, the analyses of rubber obtained by evaporation (total solids, TS) and by coagulation (dry rubber content, DRC). The results are given in Table II.

It is evident from these values that the rubber contents of the various fractions decrease greatly with a decrease in the size of the particles. Consequently, there is a definite increase in the content of serum substances with

respect to rubber present. This explains the considerable increase in the non-rubber content in the evaporated samples. In the coagulation of latex the non-coagulable substances are removed by washing, but the content of coagulable substances, notably proteins and lipides, increases greatly in the dry rubber with a decrease in particle size. It also follows that, in the fractionation of latex by centrifuging, particle size is the governing factor with regard to the composition of the resulting rubber.

The average diameter of the rubber particle can also be calculated from an actual count of the number of particles in a carefully diluted latex, assuming sphericity and a predetermined density. This was done by Langeland[11] who, by converting the results to a basis of 35 per cent DRC, obtained an average value of 0.64×10^{12} particles per gram of latex and an average diameter of 1.04 microns. It was admitted that the count number was probably too low because of ultramicroscopic particles which escaped observation. Van Gils[12] used an ultrasmicroscope and found indeed the much larger number of 1.19×10^{12} particles per ml of latex of 40 per cent DRC. Discussing these results, van den Tempel[13] points out that the use of visible light in determining average

TABLE II

RELATION BETWEEN PARTICLE SIZE AND SUBSTANCES DISSOLVED IN SERUM

				Nitrogen, %		Ash, %		Aqueous extr., %		Acetone extr., %	
Fract.	DRC	TS	TS/DRC	TS	DRC	TS	DRC	TS	DRC	TS	DRC
1	67.0	67.7	1.01	0.07	0.04	0.17	0.06	1.2	0.5	2.4	2.2
2	39.2	40.4	1.03								
3	22.0	23.4	1.06	0.44	0.17	0.72	0.08	4.2	0.7	3.8	3.7
4	15.7	16.8	1.07								
5	10.8	11.8	1.10	0.92	0.44	1.33	0.10	13.1	1.7	6.4	6.1
6	7.8	9.2	1.17								
7	6.3	7.6	1.20	1.57	0.74	2.12	0.17	20.4	3.3	8.6	8.9
8	5.0	6.5	1.28								
9	4.0	5.5	1.37	2.16	1.46	3.31	0.38	25.9	12.0	12.1	12.9
Orig.	15.7	17.0	1.08	0.59	0.30	0.89	0.10	7.3	1.5	4.4	4.5

particle size or particle size distribution in Hevea latex renders the results meaningless, as only about 40 per cent of the particles have a diameter of more than 0.2 micron. Later it was admitted that even by means of ultramethods a considerable number of very snall particles may still have escaped detection since the limit of visibility in the ultramicroscope was not as low as had been assumed previously[14].

The use of the electron microscope for this purpose was greatly improved by the introduction of the brominating process by Brown[15]. Schmidt and Kelsey[16], using this method, record the existence of a considerable number of particles having diameters down to 0.09 micron. They fractionated normal Hevea latex by creaming with ammonium alginate and preparing eight fractions (Table III). Light microscope examination of the skim layer obtained in the first creaming step, which still contained 72 per cent of the original rubber, showed only individual particles and complete absence of clustered latex particles. The corresponding cream, on the other hand, was observed to contain reversible clusters of particles which redispersed on dilution. Similar observations were made with the cream and skim obtained in the three subsequent creaming steps.

These observations and the particle size analysis of the eight creamed fractions indicate that fractional creaming of Hevea latex is preceded by selective clustering of the particles according to size.

Van den Tempel[14] investigated the contribution of the very small particles to the total number and to the interfacial area. He found that most of the particles, even in concentrated latex, are less than 0.2 micron in diameter and that they have a considerable influence on the specific interface, although they contain only a few per cent of the rubber present.

Average specific surface area and volume-surface average diameter of particles in synthetic latexes have more recently been determined by a number of workers by a soap titration method. In this case, the latex is titrated with a solution of the same soap as that already present as stabilizer, the end point being the onset of soap micelle formation in the aqueous phase. This occurs at the critical micellar concentration (c.m.c.) for the soap. Knowing the c.m.c. and the total amount of soap in the latex at the titration end point, the quantity of soap adsorbed at the rubber-water interface is found by difference. By assigning a molecular area to the adsorbed soap, the area of rubber-water interface and an average particle diameter can be calculated. Cockbain[16A] has applied this method to natural latex using sodium dodecyl sulfate as a soap. Nine different ammoniated latexes were tested with results as given in Table IV. Numbers 1–5 were concentrates, Numbers 6–8 were field latexes and Number 9 was a centrifuge skim. In general, the particle sizes are in the sequence which would be expected from the methods of treating the original field latexes. The most direct test of the validity of the method in an absolute sense would involve comparison with the results obtained directly by means of the electron mircoscope. Measurements of this kind were made on latex 7 and analysis indicated that the true specific surface area was probably slightly less than the value given in Table IV.

Table III

Particle Size Fractionation of Diluted Normal Hevea Latex
Schmidt and Kelsey[16]

Fraction	Ammonium alginate, % on aqueous phase	DRC, %			Rubber recovery in cream	Size of creamed particles, microns	
		Prior to creaming	Cream	skim		Mass median diam.	Number modal diam.
1	0.031	5.60	62.2	4.32	27.8	1.28	1.16
2	0.062	4.28	60.0	1.97	41.1	0.81	0.58
3	0.103	1.95	52.3	1.02	15.1	0.44	0.35
4	0.164	1.01	48.2	0.38	9.9	0.29	0.26
5	0.224	0.37	46.0	0.04	5.4	0.23	0.21
6	0.343	—	—	—		0.16	0.13
7	0.463	—	—	—	0.7	0.13	0.12
8	0.583	—	—	—		0.12	0.09

Ogilby[17] measured several synthetic and natural latexes by conventional electron microscope techniques and then titrated these latexes conductometrically with electrolytes at pH levels low enough to inactivate their soap stabilizers. The titration values were resolved to latex particle size by the use of the Gibbs' adsorption theory. Calculations from these titrations indicated that some of the prevailing theories regarding the surface area covered by soaps should be reconsidered.

The most recent work on the structure of the rubber particle has been done by a group of INIRO researchers including Schoon, Phoa and van der Bie[18,19,20,21]. Using a phase-contrast microscope they investigated latexes of the following plants: Hevea brasiliensis, Ficus elastica, Ficus Nekbudu, Manihot dichotoma, Castilloa nicoyensis, Manilkara balata and Cryptostegia grandiflora. Some of the larger spherical particles in these latexes seemed, even in the fresh state, to be built up from other spherical particles of much smaller diameter. Following the method of Brown[15] the latex was fixed by bromination. This showed the morphological structure of almost all clearly visible particles to be spherical, oval, or pear-shaped. (The authors point out that, as a result of the bromination process, the diameter of the particles increases by about 10 per cent. This increases the volume by about 30 per cent and conclusions about shape and size of the particles before bromination should only be drawn with the greatest caution. Another inherent danger in the bromination process is that only with the greatest care is it possible to prevent non-rubber constituents from interfering with the image of the real rubber particle.) Addition of 1–2 per cent NaOH to the latex also makes the grapelike arrange-

TABLE IV

PARTICLE SIZE DATA FOR AMMONIA PRESERVED LATEXES
COCKBAIN[15a]

Latex	Detergent adsorbed per cc rubber, mg	Specific surface areas, cm^2	Volume-surface av. diam., microns
1	6.6	8.3×10^4	0.72
2	9.5	11.9×10^4	0.51
3	8.9	11.2×10^4	0.54
4	6.4	8.0×10^4	0.75
5	11.1	13.9×10^4	0.43
6	15.0	18.9×10^4	0.32
7	10.2	12.9×10^4	0.46
8	16.1	20.4×10^4	0.29
9	42.2	52×10^4	0.12

ment clearly visible after a few days. From this study the general conclusion is drawn that all rubber particles in natural rubber latexes with a diameter of more than approximately 400 A (= 0.04 micron) are secondary particles, built up from smaller spherical particles. The value of the minimum diameter was later changed to 0.03 micron.

In more recent work the electron microscope was used on brominated latex and it was thus possible to ascertain that the highly asymmetric size-frequency distributions that are apparently present result from the existence of several size fractions each of which has a normal Gaussian distribution. Particle sizes were found to be multiples of whole numbers of either of two particle sizes: 0.058 and 0.069 micron. A possible explanation of this phenomenon is that the larger particles are formed by clustering of the smaller particles in a grapelike arrangement as observed in the phase-contrast microscope, without actual coalesence or fusing. If this concept of the existence of primary spherical particles and the structure of secondary particles can be confirmed this may lead to new points of view in regard to latex processing, both in concentrate and dry crepe production.

Much effort has been exerted in obtaining and interpreting molecular weight

data of the rubber hydrocarbon. In 1922 Staudinger started his now classical studies of natural compounds, advocating the idea that many of them consist of macromolecules, built up by polymerization of a relatively small basic unit. The rubber hydrocarbon was thus considered as a polyisoprene and earlier data on molecular weight indicated a value of 200,000–400,000, i.e., one molecule would consist of 3000–6000 isoprene units[22]. In later work this view on the structure of the rubber molecule was confirmed and various methods were employed to refine the analysis, establish the molecular weight distribution and evaluate the effect of various factors (oxygen, light, mastication) on the original molecular weight of rubber in latex as produced by the Hevea tree. Preceding this, the view was held by Pummerer et al.[23] that rubber normally exists in the form of micelles comprising more or less well-defined aggregates containing a considerable number of "chemical" molecules. However, in 1942 Gee[24] showed conclusively that the evidence in support of a micellar structure of rubber was unsound and that the rubber units are in fact true macromolecules.

Meyer and Wertheim[25] determined the limiting viscosity of crepe rubber in benzene and found an average molecular weight of 500,000 as compared to 270,000 for rubber slightly degraded by mastication. At the same time evidence was obtained in favor of an unbranched chain structure of the hydrocarbon. Houwink[26] and Flory[27] showed that the Staudinger law in its simplest form, relating intrinsic viscosity to number average molecular weight through the equation: $[\eta] = KM$ is not in agreement with experiment and both authors agreed that the correct relation is $[\eta] = KM^{\alpha}$. Carter, Scott and Magat[28] checked the validity of this relation and found $\alpha = 0.667$ in the case of natural rubber. Molecular weight was determined from osmotic pressure measurements and viscosity was measured with an Ostwald viscometer. The relation for Hevea rubber was found to correspond to: $[\eta] = 5.02 \times 10^{-4}\ M^{0.667}$ and molecular weight values of twenty-two different fractions (fractionated by precipitation with methyl alcohol from toluene solutions) ranged from 40,000 to 1,500,000, thus showing a large spread in the number of isoprene units in the rubber polymer.

Huggins[29] has demonstrated from theoretical considerations that the value of the exponent in the generalized equation: $[\eta] = KM^{\alpha}$ depends on the shape of the polymer molecule. Any factor tending to affect shape, such as chain branching, or tending to restrict the extensibility of the molecule, such as cross-linking, can be expected to reduce the value of the intrinsic viscosity per unit molecular weight. This would be reflected in a reduced value of α. Accordingly, as Bloomfield[30] points out, the value $\alpha = 0.667$ may be too high in the case of rubber fractions containing microgel, in which it is generally assumed that a certain degree of crosslinking is present.

Investigations carried out in Malaya during the period 1948–1951 by Bloomfield[30,31,32] with the object of characterizing the rubber hydrocarbon in fresh Hevea latex have led to a greater knowledge of its structure in the original state. The main questions then requiring answer were:

(1) whether rubber is already present in the form of high molecular weight polymer in the tree and, if so, whether it is a mixture of polymer homologues or of narrow molecular weight distribution;

(2) whether rubber undergoes any substantial change after leaving the tree;

(3) whether there is combined oxygen present in fresh rubber.

Two techniques developed in Malaya have simplified the problem of characterization of the rubber hydrocarbon. Firstly, McMullen[33] developed an

apparatus and technique for obtaining latex from the tree in a nitrogen atmosphere in darkened vessels, and, if desired, under sterile conditions. Secondly it was found that if fresh latex was shaken with a considerable volume of benzene a homogeneous solution was obtained within a few minutes.

The order of magnitude of the intrinsic viscosities found was generally of a high order compared with values observed in the rubber consuming countries. This was again observed in fractionation experiments, whether carried out on fresh smoked sheet after removing gel or on solutions obtained direct from latex. It was shown that low molecular weight fractions were present in the rubber and in all low molecular weight fractions with intrinsic viscosity below 1.0 positive confirmation of the presence of combined oxygen was obtained, the amount rising to as much as 1 per cent of oxygen in fractions with intrinsic viscosity below 0.5. Confirmation of the high order of molecular weight, indicated by the intrinsic viscosity, followed from the osmotic pressure measurements of molecular weight recorded in Table V.

When the technique of taking samples of latex into benzene was applied to trees representing a number of clones which had not been tapped for several years, it was immediately apparent that the latex from such trees had unusual solubility characteristics compared with normal latex. The solutions had a

TABLE V

INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS OF SOME HEVEA HYDROCARBON FRACTIONS. BLOOMFIELD

Intrinsic viscosity	Number average molecular weight	Viscosity average molecular weight
9.7	$>2 \times 10^6$	2.5×10^6
7.9	$>2 \times 10^6$	1.8×10^6
5.96 5.72	1.1×10^6	1.2×10^6
3.80 3.73	0.8×10^6	0.6×10^6
2.86	0.25–0.35×10^6	

low intrinsic viscosity frequently in the range 0.5 to 1.0; rubber deposited from them was tough and incapable of being redissolved. Osmotic pressure was too small to measure, hence the dispersed molecules were quite large. The limited swelling of this rubber in benzene indicated a considerable degree of crosslinking. Latex from these trees was believed to be a true microgel latex containing crosslinked particles of colloidal dimensions.

It follows that considerable changes must occur in the characteristics of latex and of the rubber derived from it when untapped trees are brought into regular tapping. The change from microgel latex to a latex yielding normal rubber was complete in about ten tappings (half spiral, alternate daily). During this period the inherent viscosity of solutions of the latex increased from about 1 to 4 or more, while the rubber became progressively softer.

Bloomfield concludes from these investigations that the rubber hydrocarbon as it leaves the tree is already a high molecular weight polymer with a broad molecular weight distribution ranging from several millions to well below 100,000 but containing the major part of the hydrocarbon in the higher molecular weight range. Changes in the hydrocarbon subsequent to its leaving the tree tend to be degradative, but may also involve crosslinking reactions leading to changes in plasticity. A microgel component present in the freshly tapped latex is of considerable importance in influencing the hardness of raw rubber,

but greatly complicates the interpretation of viscometric data. Evaluation by the equation: $[\eta] = 5.02 \times 10^{-4}\ M^{0.667}$ only appears to be valid for gel-free rubber fractions.

The fractionation technique used by Bloomfield was applied by Drake[34] to smoked sheet and to F rubber (a type of raw rubber developed by U.S. Rubber Co.[35])in the United Kingdom. No very high molecular weight fractions were found in the smoked sheet but the F rubber yielded a fraction of $\eta = 7.3$ and a number average molecular weight of 6×10^6. It was assumed that by the time smoked sheet has reached temperate climates the high molecular weight portion has probably been converted to gel and that F rubber, presumably because of its different method of preparation (flocculation of formaldehyde preserved latex), retains the major part of its high molecular weight material during prolonged storage.

Van Essen[36] developed a method for the rapid determination of the average molecular weight of rubber in fresh latex by using a binary mixture of toluene and pyridine as a solvent. Molecular weight was calculated from viscosity measurements using Staudinger's formula; results are therefore not directly comparable to those obtained by Bloomfield. A number of latex samples from clonal trees were investigated the same morning the trees were tapped and average molecular weights were found to range from 238,000 for Glenshield 1 to 480,000 for BD 5. Van Essen[37] also found that the molecular weight of rubber in fresh latex obtained from young parts of the tree is lower than that in latex from the trunk. The molecular weight of the rubber in the smallest particles in fresh latex is the same as that in the biggest particles. Hessels[9,10] reported that latex undergoes changes during storage which are greatest for the smallest particles, so that ultimately in old preserved latex a final stage is reached in which the molecualr weight of rubber in the smallest particles is lower than that in the bigger particles.

Schulz, Altgelt and Cantow[38] used light scattering to work out an experimental method in which crepe rubber, prepared under conditions excluding oxygen and light, was dissolved and the solution purified for optical measurements using an ultracentrifuge. By determining the molecular weight, the diameter of the coiled molecule and certain thermodynamic quantities it was possible to obtain information on branching of the rubber molecule. The average molecular weight was 1.3×10^6, in agreement with Bloomfield's data, and the end-to-end distance of the coil was 1750 A. These results indicate that the rubber molecules, as present in latex under the conditions described, are unbranched or only slightly branched. In later work, Altgelt and Schulz[39] reported the presence of microgels in natural rubber solutions prepared with exclusion of oxygen and estimated the diameter of these microgels at above 4000 A. The mean molecular weight of the sol portion was 1.03×10^6. These results could be confirmed in sedimentation experiments with the ultracentrifuge.

III. SURFACE CHEMISTRY OF THE RUBBER PARTICLE

Concentrated suspensions, such as natural latex, are known to be stable only if a sufficient amount of an emulsifying agent is present to form a film over the particle surface. As far back as 1903 Weber[40] suggested that adsorbed proteins assume this role in Hevea latex. Isoelectric point values reported for Hevea latex all lie within the range of pH 3.0–5.0, characteristic of many proteins. Later it was shown by Kemp and Twiss[41] that the isoelectric point of their latex

samples was identical with the isoelectric point of the mixture of proteins in the latex. Further evidence that proteins are responsible for the stability was furnished by coagulation experiments, which indicated that many typical protein precipitants could likewise coagulate Hevea latex[42]. Bondy and Freundlich[43] subjected the serum of ammonia-preserved Hevea latex to fractional precipitation and isolated two proteins, A and B. Protein A is insoluble in water and in alcohol with an isoelectric point at pH 4.55. Protein B is soluble in water and in 70 per cent alcohol, with an isoelectric point at pH 3.9. They next compared electrophoretic mobility curve of the latex suspended in the same buffers with that yielded by quartz particles immersed in a 1:1 mixture of the two proteins and found the two curves very similar to each other. The electrophoretic behavior of the rubber globules in the latex indicated that the adsorbed film is normally provided by protein A.

This early evidence makes it clear that the surface chemistry of the rubber particle and the protein chemistry of Hevea latex in general are closely associated. For this reason the latter will be briefly discussed in this section. However, although in normal circumstances the exposed surface of the protective layer is doubtless of protein character, special conditions may arise in preserved or compounded latex, leading to removal of part of the protein film or to partial or complete replacement by a film of other composition. At certain degrees of dilution and pH of the serum the protein of ordinary ammonia preserved latex may, for instance, become partly replaced by natural fatty acid[41]. During the last twenty years most of the work in this field has been directed towards a better understanding of the nature of these components and of the part they play in compounding and processing procedures.

Several investigations have been made of the amino acids derived by hydrolysis from the proteins of rubber and latex serum, while others have been concerned with the amino acids present as such in latex. McGavack and Rumbold[44] isolated d-alanine from latex serum and secured some evidence of the presence of phenylalanine. Whitby and Greenberg[45] found the following seven amino acids in the serum: tyrosine, l-leucine, d-iso-leucine, d-valine, d-arginine, l-aspartic acid and i-proline. Indications were also obtained of the presence of phenylalanine. It is interesting to compare these findings with the results of the examination of the amino acids obtained by hydrolysis of protein. Belgrave[46] obtained evidence of the presence of glycine and proline in proteins obtained (a) from latex serum by precipitation with alcohol, and (b) from rubber by exhaustive extraction with benzene. Later work by Belgrave[47] on the former protein indicated the presence, in addition, of arginine, cystine, histidine and lysine. Midgley, Henne and Renoll[48] obtained the following from protein isolated from rubber: glycine, proline, arginine, histidine, lysine, leucine, aspartic acid and a representative of the group comprising alanine, phenylalanine, hydroxy-proline and serine. They state that the following amino acids are definitely absent: cystine, glutamic acid and tyrosine. Subsequent authors, however, working with protein isolated from rubber or latex in different ways, have identified these three amino acids in hydrolysates.

In protein obtained from latex serum by precipitation with ammonium sulfate, Altman[49,50] identified and estimated proline, arginine, histidine, leucine, aspartic acid, alanine, dihydroxyphenylalanine, tyrosine, glutamic acid, hydroxyproline and valine. Tristam[51] analyzed protein obtained by extraction of dried, fresh latex for the following nine amino acids, all of which were present, and which in total constituted about 50 per cent of the protein: arginine, histidine, lysine, aspartic acid, tyrosine, glutamic acid, cystine, methionine and

tryptophan. A protein was also isolated from crepe rubber and analysed for amino acids. The results indicated that this protein was of the same composition as the protein extracted from dried latex[52]. Whitby and Greenberg[45] also examined the heat-coagulable protein of latex serum which led to the isolation from its hydrolysate of glycine, proline, aspartic acid, glutamic acid and tyrosine, and gave evidence of the presence, in addition, of histidine, arginine and lysine. Table VI summarizes the results of investigations made to date on the isolation and identification of the amino acids of rubber, latex and latex serum. It shows that of the more common amino acids only serine and threonine have so far not been detected in latex protein or in the serum.

Protein fractionation has indicated the complicated nature of the latex proteins. Three fractions were isolated by Kemp and Straitiff[53] from fresh latex and from ammoniated latex by the method of Bondy and Freundlich[42]. Color and precipitation reactions indicated that these proteins were conjugated glyco-

TABLE VI

AMINO ACIDS IN LATEX AND FROM LATEX PROTEINS

	Authors					
Amino acid	43	44	45	47	48	50
Glycine	—	+	+	+	—	—
Alanine	+	—	—	—	+	—
Serine	—	—	—	—	—	—
Cystine	—	—	+	—	—	+
Threonine	—	—	—	—	—	—
Valine	—	+	—	—	+	—
Methionine	—	—	—	—	—	+
Leucine	—	+	—	+	+	—
Isoleucine	—	+	—	—	—	—
Phenylalanine	+	+	—	—	—	—
Tyrosine	—	+	—	—	+	+
Dihydroxy-phenylalanine	—	—	—	—	+	—
Proline	—	+	+	+	+	—
Hydroxyproline	—	—	—	—	+	—
Tryptophane	—	—	—	—	—	+
Aspartic acid	—	+	—	+	+	+
Glutamic acid	—	+	—	—	+	+
Arginine	—	+	+	+	+	+
Lysine	—	+	+	+	—	+
Histidine	—	+	+	+	+	+

proteins. Those recoverable from fresh latex differed in composition from those to be found in ammoniated latex and the former are not so easily coagulated. The mechanism of the stabilization of latex was explained by Kemp and Straitiff on the basis of an intimate relationship with the electric charge induced by proteins on the surface of the rubber particle. The amphoteric character of these proteins would give a zwitter-ion effect and this in turn would serve to explain the mechanism of coagulation.

A more detailed electrophoretic analysis of the proteins in unammoniated serum was carried out by Roe and Ewart[54] who demonstrated the presence of seven electrophoretically distinct protein components. They also made the interesting observation that ammonia preservation rapidly alters the electrophoretic behavior of the native components of latex serum and reduces the number of resolvable components from seven to two. Archer and Sekhar[55] separated the aqueous serum phase of unpreserved latex in two ways: (a) by

high-speed centrifuging and (b) by prolonged freezing at −25°. The protein contents of the serum were approximately 18 and 13 per cent, respectively. In both types of serum, seven electrophoretically distinct protein components were detected, with only two readily resolvable after treatment with dilute ammonia solution for 15 days, thus confirming Roe and Ewart's results. One of these was found to be a major component of the unammoniated serum. This component was isolated by Archer and Cockbain[56] by an isoelectric precipitation method. Analytical and solubility data indicated that it is a globulin lacking, non-protein, prosthetic group. To avoid confusion between the lettering and numbering systems of different workers, the authors propose that this protein be referred to as the α-globulin component of latex serum. It appears to correspond to component V in the nomenclature of Roe and Ewart[54] and was almost certainly the main constituent of "protein A" described by Bishop[57], Kemp and Straitiff[53] and Bondy and Freundlich[43].

The other protein that survived hydrolysis by ammonia was found to be highly basic; it was recently named *Hevein*[58]. Paper chromatographic analysis of the α-globulin shows it to be built up from fifteen different amino acids which have been identified. *Hevein* is also built up from fifteen different amino acids, fourteen of which are the same as in α-globulin, although in different relative proportions, and the other is cystine which is present in remarkably large amounts.

These latest developments in the protein chemistry of Hevea latex are considered of great fundamental value; they also have an important practical bearing in that the amino acids produced by ammonia hydrolysis effect the stability and processing properties of the latex and latex concentrate. Continued studies of the chemistry of cystine in ***Hevein*** may lead to a better insight in the development of certain odors in latex concentrate, inasmuch as the sulfur containing cystine may be the source of one component, hydrogen sulfide.

Considering the interrelationship of the various surface active materials in latex, the behavior of fresh and ammonia preserved latex and also of artificial dispersions in which the dispersed particles are covered by protective layers of the protein constituents of the serum, has provided evidence that the external surface of the globules has similar chemical nature in all three cases[59]. However, the protective layer is not necessarily of uniform composition throughout its depth but probably orientated with respect to the rubber-water interface. Furthermore, it is believed by some[60] that the protein on the globules is actually present in the form of a "protein-lipin" complex. As electrophoretic examination throws light only on the nature of the surface presented to the aqueous phase, the experimental demonstration of the protein character of the protective coating would be quite consistent with this possibility and would indicate that the molecules of any such complex are orientated with their protein characteristics exposed externally.

The postulated existence of the "protein-lipin" complex can be made to afford a tentative explanation of certain distinctions between fresh and preserved latex. When brought to the isoelectric point of the protein, fresh latex undergoes a slow thickening until, after some hours, it forms a uniform reticular mass of coagulum. In contrast, the uniform acid coagulation of ammonia preserved latex is difficult, the addition of acid resulting in immediate local coagulation which tends to prevent uniform distribution. The slow coagulation rate and the formation of a uniform, reticular mass of coagulum with fresh latex may be associated with an orientated adsorbed layer of the "protein-lipin" complex. In ammoniated latex, on the other hand, the presence of the alkali

may have resulted in the fission of the "protein-lipin" complex, the lipin products passing into the serum and the protective layer becoming entirely protein in character. This may also provide an explanation for the observation that whereas the adsorbed interfacial layer on the globules in fresh latex is not readily desorbed, the protein adsorption in ammonia preserved latex is readily reversible[41]. Baker[61,62] developed a method for determining the distribution of the non-rubber substances between the rubber-and-water phases in latex and applied this method to the study of the distribution of nitrogen and materials extractable with acetone. His results indicate that changes in the chemical composition of ammoniated latex are due to the joint action of enzymes and ammonia tending (1) to liberate and degrade proteins, causing those in the adsorbed layer round the particles in part to pass into the aqueous phase and (2) to liberate fatty acids which accumulate as ammonium soaps at the rubber-water interface. Process 1 tends to decrease while process 2 tends to increase the resistance of latex towards coagulation by acid. The displacement of protein by soaps at the interface occurs mostly during the first 50 days after ammoniation. It was further shown that the nitrogen associated with the rubber phase is of two different types, a small amount (about 0.02 per cent) being independent of particles size and consequently distributed throughout the mass of the rubber, whereas the remainder is a function of particle size, replaceable by surface active materials such as soaps, and is, consequently, situated at the surface of the particles. The exact arrangement of the surface-active substances is not known, but it was suggested that they exist as a complex film which may become a double layer with the hydrophobic lipoid portion next to the rubber phase and the hydrophilic proteins and soaps on the outside. This duplex layer is unlikely to be more than about 40 A thick, assuming that the lipoid portion is thinner than a fatty acid monolayer, which is known to be about 25 A, and that the thickness of a compressed film of latex protein is about 15 A. The latter was shown by Wren[63] applying the Langmuir trough.

Baker's experiments showed that to replace the protein entirely by hydrolysis, at least five times as much soap is required and that the quantity of fatty acid present in ammonia preserved latex is not much more than 1 per cent. There is insufficient fatty acid present in latex, therefore, to replace all the protein on the globule and, as the substances forming the surface layer are hydrolyzed, the amount of adsorbed material per unit area of the rubber-water interface will decrease, allowing the interfacial film to expand, with consequent lowering of surface pressure and probably of the ζ-potential. This is in agreewith the decrease in resistance to coagulation observed in latex on storage. If however, sufficient fatty acid is added to latex, a fatty acid-protein complex will first be formed, followed by dispersion of the protein layer, the fatty acid also penetrating the lipoid layer. In consequence, the surface of the particle would become more hydrophobic and the ζ-potential would be increased, giving an increased resistance to coagulation. This theory, developed by Wren and Baker, elaborating upon older concepts, gives an elegant and ready explanation of various phenomena in the behavior of latex.

A different aspect of the surface chemistry of the rubber particle was dealt with by Belmas[64,65]. His work is devoted to metal components, including potassium, sodium, calcium, magnesium and iron, which are capable of influencing, when in soluble form, the colloidal behavior of latex and more in particular to their adsorption equilibria.

The existence of adsorption equilibria as a function of the dilution of latex and comparison of the experimental curves with the isotherms of Freundlich

and of Langmuir showed that, in the case of latex, adsorption is not a simple phenomenon. At least two different processes seem to be involved: (1) electrosorption of the metallic cations by the negative surface of the rubber particle and (2) indirect adsorption, whereby the metal is bound in a slightly dissociable form to an organic anion which is itself strongly adsorbed. This would explain the much weaker adsorption of the alkali metals whose salts are in general more easily dissociated than those of the alkaline earth metals. Results obtained for metals added to the latex in the form of soluble salts led to the same conclusions.

Measurement of the adsorption equilibria for samples containing different DRCs show that, the smaller the proportion of dispersing phase to dispersed phase the higher is the adsorption. This phenomenon, which is evident with alkali metals as well as with alkaline earth metals, can be explained by the increase of the charge on the particles when the latex is diluted. An examination of the critical adsorption values for the different metals studied confirmed the fact that the behavior of latex with salts is that of a mixed sol with both hydrophilic and hydrophobic properties.

So far, it has usually been assumed that the surface of the rubber particle, free from adsorbed soaps and proteins, consists of plain hydrocarbon. Until recently it has been impossible to investigate the properties of this surface for the removal of the surface-active agents results in coagulation. However, latex particles can now be obtained in a hard and non-tacky form by hydrochlorination and crystallization according to the method of van Veersen and Schuur[66,67]. The various surface active agents can then be removed by filtering, washing, and extraction with organic solvents, without the loss of surface by coagulation. Dispersions of these hydrochlorinated particles in plasticizers were investigated by Schuur[68] and the rheological properties of these resins showed that the surface of the rubber is not plain hydrocarbon, but that its properties and chemical composition depend on the type of latex and on the way the latex was treated and stored prior to hydrochlorination. The results could be explained by assuming that carboxyl groups are bound to surface polymer molecules of the rubber hydrochloride particles. If the presence of free carboxyl groups in the surface can be confirmed for the untreated rubber particle, this may be of interest for the further development of the surface chemistry of the rubber particle.

IV. ELECTROPHORETIC MOBILITY

One of the main causes of the stability of colloidal suspensions is an electrical charge on the surface of each particle. Inasmuch as particles of like charge repel each other, this force prevents the aggregation of two or more particles and so tends to stabilize the colloidal suspensions. Natural rubber latex does not differ from other colloidal suspensions in this respect. As early as 1906 Henri[69] demonstrated that the particles in Hevea latex migrate in an imposed electric field to the anode, i.e., the particles carry a net negative charge. A possible explanation of how the latex particle becomes charged is that the protein adsorbed on the rubber hydrocarbon is joined to the latter by means of only a few groups of the large protein molecule. The other groups are still free to act as they would in an ordinary protein solution. Many proteins can ionize both as acids and as bases much in the same manner as do amino acids. The kind and extent of this ionization depends on the H-ion concentration of the solution. In a highly basic medium the protein molecule, while adsorbed on the rubber hydrocarbon, can thus act as an acid with the H-ions in solution,

charging the particle negatively with its anions. In an acid medium the protein would act like a base, yielding OH-ions to the serum and leaving a positively charged cation adsorbed on the rubber. At some stage between the acid and basic solutions, the ionization of the protein would be as much acidic as basic and the particle would have no net charge. This is known as the iso-electric point[1].

As pointed out in the previous section, soaps may also form a part of the protective layer and, inasmuch as they are ionized, could bring about an electrical charge. The effect of soap addition to ammonia-preserved latex on its stability will depend on its type. "Anionic" soaps can be added without risk of flocculation to such latex and, if there is sufficient concentration, allow alka-

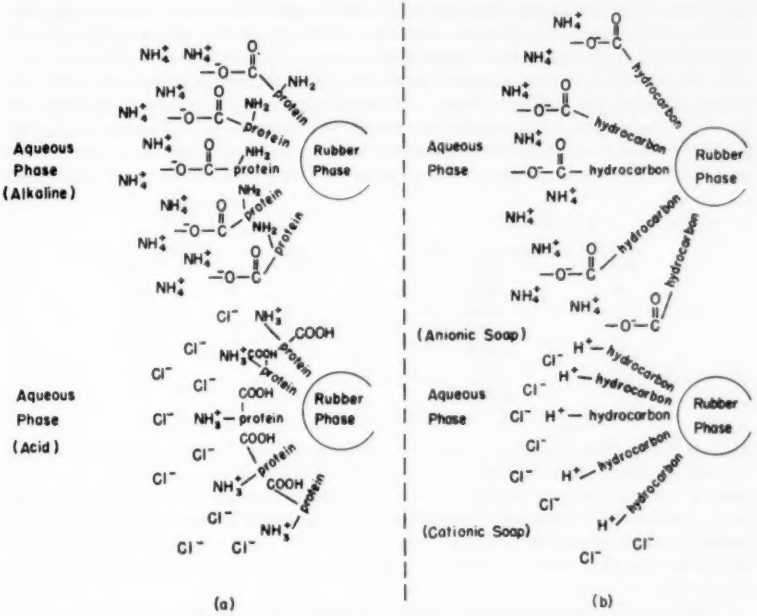

FIG. 1.—Alkaline and acid rubber latex dispersion. Stabilizer (a) protein, (b) soap.

line and acid dispersions to be obtained. "Cationic" soaps, on the contrary, as pointed out by Blow[70], flocculate such latex. It is possible, however, by addition of a quantity in excess of that which produces flocculation, to produce stable dispersions which can be rendered alkaline or acid. These points are further elucidated by the diagrams in Figure 1, slightly modified after Blow[71]. This author developed a method and apparatus for determining the electrokinetic potential by measurement of the cataphoretic velocity of the particles. In the case of rubber particles in latex this was done in the presence of cationic and anionic soap. It was found that the cationic soap is more adsorbed in alkaline solution and the anionic soap in acid solution.

An early review of the electrokinetics of rubber latex is given by Hauser and

Bender[72] in relation to electrical coagulation, electro-deposition, electrical concentration and the rubber particle surface layer. Results of experiments on catophoretic velocity, H-ion concentration and specific conductance indicated some inter-relationships and showed the influence of buffer solutions and preservative alkalies. In a more recent review Génin[73] discusses the fundamental principles of electrophoresis, its mechanism and its practical applications in the electro-deposition of rubber particles.

A set of observations made by Twiss, Carpenter and Amphlett[74] with dialyzed Hevea latex gives some interesting additional information on the electrical behavior of the rubber particle. If a series of portions of ammonia-preserved latex are subjected to graded alteration in pH, it is found that coagulation occurs over a range from 5.75–2.0. If on the other hand, the same latex has first been submitted to dialysis through a collodion membrane, the range of coagulation is much less wide; so sharp indeed is the coagulation point (pH approximately 4.3) that unless the addition of acetic acid is effected cautiously it is easy to overshoot the iso-electric point and to pass unintentionally to the condition of a stable positive latex. This result has a possible parallelism in Blow's[71] observation that purification of Hevea latex by centrifuging or dialysis facilitates the avoidance of coagulation when a cationic soap is added for reversal of the electric charge. The results of Twiss et al. have been confirmed

TABLE VII

Age, days	Conductivity $\times 10^3$, 28° C
0	4.52
1	4.96
2	5.13
4	5.25
16	6.17
25	6.83
43	9.10

TABLE VIII

Age, days	Conductivity $\times 10^3$, 28° C
0	0.585
2	0.739
3	0.767
6	0.867

by van Gils[75] who, on attempting to coagulate dialyzed latex for a DRC determination, found that it did not coagulate. Coagulation occurred, however, when a few milliliters of NaCl solution, KCl solution or ethyl alcohol were added to the acid. It was also confirmed that for ordinary latex the coagulation range is much wider than for dialyzed latex and that addition of salts widens the range for dialyzed latex. This is explained on the basis of the potential lowering effect of salts.

Conductivity measurements made by van Gils[76] on ammoniated and dialyzed latex throws some more light on the structure of the electric double layer. On storage of latex the conductivity continually increases as shown by Table VII, with the greatest change occurring during the first two days. The same happens in dialyzed latex although the conductivity is much lower, as can be expected (Table VIII).

In latexes, preserved with ammonia and sodium pentachlorophenate, conductivity increases much less than in fully ammoniated latexes. If the large changes may be attributed to the action of micro-organisms, this shows the efficacy of this preservative system. The slow constant rise is possibly due to chemical effects, i.e., hydrolysis.

Ammonia has a great influence on conductivity in dialyzed latex, but since the conductivity of ammoniated latex is less than the sum of the individual conductivities (latex and aqueous ammonia), a great deal of ammonia must be

adsorbed on the rubber particles. When ammonia is added to fresh latex or to serum prepared by freezing latex, the conductivity curve shows a bend caused by precipitation of magnesium ammonium phosphate. Conductivity measurements in dialyzed latex after adding salts show that the salts are partially adsorbed by the rubber particles; divalent calcium ions especially are strongly adsorbed. Similar results were obtained by Belmas[65].

The relationship between electrophoretic mobility and pH has been determined by Roe and Ewart[54] for five of the seven protein components found in unpreserved total latex serum as shown in Figure 2. The wide distribution of isoelectric points on the pH scale is a matter of interest. Since two of these isoelectric points occur at pH 7.2 and pH 9.7, the persistence of positively charged protein components at high pH values is demonstrated. This may account for the known stability of fresh unpreserved latex toward the addition of acid, whereas the negative components stabilize with respect to added alkali.

The effect of seasonal and clonal variations, latex aging, ionic strength, pH, and the presence of added materials on the electrophoretic mobility of the rubber particle in fresh Hevea latex was studied by Bowler[77]. All mobility meas-

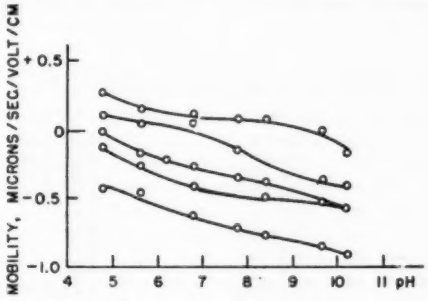

FIG. 2.—Mobility-pH curves for five protein components of latex serum.

urements except those after various aging periods were made by allowing 3 mls of latex to flow directly from the tapping cut of the tree into 500 mls of boiled distilled water 5 minutes after the flow of latex had started. The variation of mobility with pH was determined for a series of clonal trees and one seedling tree. In all cases the curves were typical of those for proteins, the only important difference from tree to tree being a slight displacement in the curve along the pH axis. The isoelectric points for several clones are shown in Table IX. They indicate variation from clone to clone, a small but definite variation from tree to tree within one clone and probably a very small daily variation for one tree. All the isoelectric point values are grouped around 4.3 except those for the first War 4 tree and those for the AV 152 trees and the seedling tree. These variations in turn indicate small but measurable differences in the nature of the rubber particle surface.

No seasonal variations were found in samples taken during the wintering period (February) and after refoliation (April). Addition of ionic material decreases the mobility very sharply at first, then less rapidly at higher ionic strengths, following a logarithmic relationship very closely. In order to determine a possible relationship between mechanical stability (MS) and mobility,

samples of War 4 latex (low MS) and PB 186 (high MS) were obtained and tested immediately after concentration and after aging periods of 30 and 90 days. Despite the very much greater MS of the PB 186 concentrate there was no significant difference in mobility between the two clones. For both clonal concentrates, the mobility increases in the high pH region with the age of the latex, probably as a result of hydrolysis of esters of high MW fatty acids with the consequent formation of ammonium soaps. These charged soap anions will be adsorbed on a portion of the rubber particle surface, displace proteins or react with them to form a soap-protein complex. This increase in mobility with aging becomes less marked at lower pH values, where the soaps are less readily adsorbed.

It was evident that there is no useful correlation between mobility in measurements of this type and MS. This was confirmed by testing samples preserved with sodium pentachlorophenate. Despite the fact that the SPP preserved sample had a MS of 2430 seconds against 480 seconds for the ammonia preserved sample the two latexes had an identical mobility-pH relationship. If the mobility is considered to be a function of the electrical charge on the rubber particles and of the ionic atmosphere in which the particles exist, then the reason for this lack of correlation may be sought in other properties such as

TABLE IX

ISOELECTRIC POINTS OF LATEX FROM INDIVIDUAL TREES. BOWLER[77]

Tree No.	Clone	Isoelec. point
1	War 4	4.50, 4.62
2	War 4	4.36, 4.36
3	PB 186	4.39, 4.31
4	PB 186	4.23, 4.25
5	AV 50	4.30
6	BD 10	4.30
7	AV 152	4.17
8	AV 152	4.04
9	Seedling	4.24, 4.20, 4.08

viscosity or particle size. The most fruitful source of information on this subject in the future will probably be chemical investigations of the proteins associated with both the rubber particle and with the serum, such as recently carried out by BRPRA workers[58].

A new method of concentrating and purifying latex, known as electro-decantation, is based on phenomena observed by Pauli and his co-workers[78,79,80,81] and by Stamberger[82] on the behavior of colloidal sols when subjected to electro dialysis. It was found that in purifying sols, such as silicic acid and serum-albumen by electrodialysis between vertical semi-permeable membranes, superimposed layers of different degrees of concentration were frequently obtained; the more concentrated layers were uppermost or the reverse, according to the relative densities of the sol and the dispersing medium.

It is suggested that this stratification is the result of the combined influence of the electrical potential and gravitational forces under suitable conditions. The influence of the electric field causes the colloidal particles to concentrate at the membrane surface; but if this influence is not too great, the gravitational force will prevent deposition on the membrane and cause the concentrated layer of particles to move upward or downward along the surface of the membrane. At the same time the sol at the other membrane becomes more dilute and moves

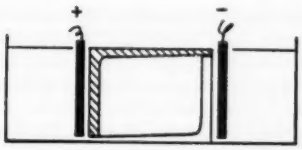

FIG. 3.—Formation of latex layers in electrodecantation cell.

in a direction opposite to that of the stream at the first membrane, and eventually the dispersions of different concentrations spread out through the cell liquid in horizontal layers which can be decanted[83].

This principle of operation, when applied to rubber latex, causes a similar separation, except that the rubber particles, being lighter than the serum, form a more concentrated layer on the surface and the clear or almost clear layer forms below. This is shown diagrammatically in Figure 3, taken from a paper by Stevens[84].

It will be noted that whereas the efficiency of creaming agents depends on their ability to increase the unit size, the electro-decantation process depends on the formation of denser or lighter layers containing massed particles. This latter process differs from creaming in that it not only causes the particles to accumulate in a denser layer on the surface, but also causes the serum to form as a relatively rubber free liquid underneath[85].

Tests showed that the lower the initial concentration of the latex and the electrical potential employed, the more efficient the separation, but at the cost of a progressive reduction in the layer formation. It was found, however, that if the current is periodically reversed during the process, potentials which would normally cause deposition could be employed, and thus the rate of separation could be increased without fear of membrane deposition.

The migration velocity of the particle depends on the magnitude of the charge on its surface and if the dispersion is near the isoelectric point, little separation occurs. It is therefore sometimes useful to increase the charge where possible in order to obtain a high rate of separation with low current consumption. In the case of rubber latex this can be effected by increasing the ammonia content. Polar substances which are also emulsifying agents have similar effects. Other suggested aids are long-chain compounds containing hydrophilic groups such as diglycol stearate, sorbitol monostearate, etc.

TABLE X

COMPARATIVE PROPERTIES OF CENTRIFUGED AND ELECTRO-DECANTED LATEX. MURPHY[86,87]

	Once centrifuged	Once electro-decanted	Twice centrifuged	Twice electro-decanted
Alkalinity (% NH_3)	0.63	0.59	0.67	0.66
Total solids, %	61.3	61.4	61.7	61.8
DRC, %	59.7	59.8	61.5	61.5
Ash, %	0.45	0.40	0.14	0.14
Nitrogen, %	—	—	0.22	0.23
Color of latex	Grade 1	Grade 1	Grade 1	Grade 1
Color of film—Lovibond units				
unaged	1.5	1.0	1.0	1.0
aged 16 hrs/95° C	2.5	2.5	1.25	1.5
Z.O.T. stability	64	63	14	15

Special apparatus has been developed for this process and the efficiency and speed of concentration have been considerably raised by improvements in design. Thus the number of diaphragms between the electrode compartments was greatly increased and in practice as many as 200 membranes may be used in a single unit.

A comparison of the creams obtained by centrifuging and electro-decantation is given by Murphy[86,87] and is reproduced in Table X.

The differences between centrifuged and electro-decanted latex in the properties tested are clearly negligible but, according to other reports, there are some differences between the two types. It is claimed that in actual practice only a small portion of the sludge is removed by electro-decantation whereas centrifuged latex is essentially free of sludge. It is further claimed that electro-decantation does not remove nearly as many of the yellow colored particles (Frey Wyssling globules) from latex as do the modern centrifuges and finally, the high recoveries claimed for the concentrate seem difficult to obtain. It is probably for these reasons that during recent years electro-decantation has lost some of its appeal. As usual with new processes, there is an array of patents in different countries covering the process and improvements thereto[88–94].

V. COLLOIDAL STABILITY

Colloidal stability is primarily a problem in surface chemistry and it is by more detailed information, such as given in the previous sections, that a fuller understanding of the behavior of Hevea latex will be most readily obtained. Following classical theory, its stability has been attributed mainly to three factors—the structure of the interfacial film, the electric charge and the degree of hydration. Some aspects thereof that have not been mentioned before will be discussed briefly in this section.

Little is known about the hydration of the rubber particle but it is generally assumed that the coagulation of latex by solvents with a high affinity for water (acetone, alcohol, etc.) is due to dehydration of the inetrfacial soap-protein film. As regards the mechanism of stabilization by hydration, it has been postulated that a layer of water, several molecules thick, can be "bound" at the interface, thereby promoting stability by a mechanical "buffer" action during collision of the particles[95]. Before this explanation is accepted, more information is needed concerning the physical properties of "bound" water at interfaces.

Another influential factor in latex stability, more in particular the chemical stability in manufacturing processes for molded articles, is called "thermosensibility". Naturally occurring but slow hydrolytic reactions in the interfacial film result in a degradation after prolonged storage that gives a heat sensitized latex after addition of zinc oxide. Lepetit found that, working with a six year old concentrate, the sensitized compounded latex could be kept for several weeks provided the zinc oxide is free from ionizable impurities[96]. Protein hydrolysis can also be accelerated biochemically, most practically by the addition of trypsin[97,98]. This produces mixtures which gel quickly at ordinary temperatures and are suitable for the manufacture of molded articles. According to Lepetit[99], this involves the mutual effect of two actions, a decrease in stability of the rubber phase (by protein degradation) and an increase in ionic strength of the serum (by release of amino acids). Solubilization of proteins can also be accomplished by subjecting the latex to the activity of such enzymes or bacteria as are naturally present in fresh latex. Under certain specific conditions that would lead to partial coagulation at normal temperatures and the

remaining latex could be used for the manufacture of a low ash, low protein rubber with a low adsorption capacity for water[100].

If normal ammoniated latex is subjected to extensive dialytic treatment the ash content of the total solids from the latex can be lowered considerably, approaching a value of 0.1 per cent. The mechanical stability of such a latex would decrease and the chemical stability would increase, as found by Kemp and Straitiff[53].

Spontaneous coalgulation of Hevea latex was explained by van Gils as"soap coagulation"[101]. He found that fresh latex coagulated on addition of sodium salts of fatty acids or sulfonic acids. The coagulating power of these soaps is restricted to a certain concentration range and the breadth of this range depends on the magnesium and calcium contents of the latex. Latex which has been freed from these ions by dialysis does not show this coagulation. The explanation of this kind of coagulation is that when soap is added the fatty acid ions are strongly adsorbed on the rubber particles with displacement of part of the proteins. In this way the protein stabilized particles are transformed into soap stabilized particles. However, these particles are not stable in a liquid containing Mg^{++} or Ca^{++} ions, hence they coagulate. Similarly, it was found that spontaneous coagulation depends on the Mg^{++} and Ca^{++} content of the latex. Latex freed from these ions by dialysis does not coagulate spontaneously and can be kept fluid for days. In actual practice it is not necessary to dialyse the latex. The addition of a small amount of NH_3 is sufficient to precipitate the Mg^{++} ions in the form of magnesium ammonium phosphate. Probably Ca^{++} can also be precipitated although it is usually present in much lesser amounts than Mg^{++}. It is thus considered that spontaneous coagulation of Hevea latex cannot be entirely attributed to the formation of acidic compounds but that as soon as the latex leaves the tree, lipids and glycerides form fatty acid ions which combine with Mg^{++} and Ca^{++} ions and lead to coagualtion.

Magnesium plays an important part in the stability of Hevea latex. In concentrate production from ammoniated latex, magnesium is removed by centrifuging as magnesium ammonium phosphate but only in so far as there is sufficient ionic phosphate present for precipitation. In some latexes, however, there is an excess of magnesium which can remain and not only reduce the mechanical stability of the final concentrate but also be responsible for excessive sludge build up, the latter as a result of a gradual release of phosphate from phospholipids. The remedy in such cases would be to add a soluble phosphate to the field latex prior to centrifuging[102,103].

Clone Glenshiels 1 (G 1) is a consistent yielder of unstable latex. The instability was described by Paton[104] for G 1 concentrate from Johore as well as from other widely distributed areas in Malaya and from Sumatra. Paton found that crepe rubber prepared from fresh untreated G 1 latex had an alcohol soluble phosphorus content much less than normal. Madge, Collier and Peel[105] found the Mg content of concentrate made from G 1 latex to be unusually high in comparison with average concentrate. They demonstrated that the MS was greatly improved by phosphate treatment and, also that the abnormal gelling properties of G 1were corrected by phosphate. A further effect of phosphate treatment is to reduce the abnormally high viscosity of G 1 concentrate. A marked improvement in MS and gelling characteristics could also be brought about by almost completely interchanging the serum of G 1 concentrate with that of a seedling latex[106].

Resing and Lunshof[107] investigated concentrate from polyclonal latex from trees tapped for the first time and tried to correlate concentrate properties with

the composition of the latex. The period of investigation included the wintering season and it was found that during that time the inorganic phosphorus content of the latex was very low. As is well known, MS values are usually lower during wintering and, although Resing and Lunshof found no evidence of excess magnesium during this period, data collected in Liberia indicate that phosphate requirements in treatment of field latex during wintering are higher[108].

The chemical stability of Hevea latex usually means the stability to thickening from zinc oxide. When zinc oxide is added to Hevea latex containing ammonia, the viscosity of the latex usually increases, due to the solubilization of the zinc oxide and the resultant formation of positively charged complex ions, which decrease the colloidal stability of the latex. Van den Tempel[109] has shown that the solubility of zinc oxide in Hevea latex at a given pH is proportional to the product of the concentration of ammonia and the ammonium salts present in the serum.

Kraay and van den Tempel[110] found that zinc oxide destabilized ammonia preserved latex partially by ionic adsorption of positive zinc or zinc amine ions on the negatively charged latex particles, and partly through the formation of insoluble zinc soaps from the adsorbed ammonium soaps on the latex particles. When the natural higher fatty acids on the latex particles were displaced by a surface active material which does not form an insoluble zinc soap, such as Igepon-T, the latex did not gel when heated with ZnO and NH_4Cl. By displacing the Igepon-T with ammonium oleate, the original rapid gelation was restored. Newnham[111] also emphasized the importance of zinc soap formation during the gelling of latex.

On the basis of these observations Dawson[112] developed a zinc oxide viscosity (ZOV) test for determination of chemical stability. In this test the stability is determined by measuring the increase in viscosity with time (Brookfield Viscometer) after treating the latex with soap (potassium oleate), a sensitizer (ammonium sulfate) and zinc oxide. This ZOV test has proven to be simple, rapid, sensitive and reproducible and has been valuable in studying the effect of aging latex at various temperatures, ammonia concentration, preservative and variations in serum solids. It has also been used in predicting the processing behavior of Hevea latex in the production of foam rubber and other rubber products.

The colloidal stability of Hevea latex can also be assessed in terms of mechanical stability. The testing method for determination of MS is based on high speed stirring of the sample under standardized conditions. Rubber particles start to agglomerate as soon as the peripheral speed of the agitator reaches a certain minimum value. Progressive flocculation continues until mechanical coagulation occurs. The end point is defined as the time in seconds required for the first flocs to appear. If the shear is constant, the time is proportional to the mechanical stability. Test results depend critically on size, total solids and temperature of the sample. Methods have been published by Jordan, Brass and Roe[113], Novotny and Jordan[114] and Dawson[115].

VI. YELLOW PIGMENT, FW GLOBULES AND VISCOIDS

It is a well known fact that Hevea latex is on occasions distinctly yellow in color and that there is considerable variation in the color intensity of different latexes. The color persists in the raw product when latex is converted into crepe. Even in cases where the latex appears to be white when freshly tapped, crepe prepared from such a latex is generally of a distinctly uniform yellow tint.

A very considerable variation in color intensity of crepe prepared from latexes obtained from different clones has also been observed, the color in some cases ranging from a faintly discernible yellow to a bright canary yellow.

In regard to the composition of this yellow pigment Eaton and Fullerton[116] found that it possessed properties characteristic of the hydrocarbon carotene. However, after the complex nature of this pigment was discovered (alpha carotene, 1931; gamma carotene, 1933) the question could still be raised of the chemical constitution of the carotenoid pigment in Hevea latex. Koch[117] investigated the nature of the pigment by extracting a sample of canary yellow first fraction crepe with cold acetone and analyzing the extract by chromatographic and spectrographic methods. Chromatography separated the pigment into three fractions, of which the main one was unambiguously identified as beta carotene by its absorption spectrum. Two other fractions, smaller in bulk, were less completely characterized but they were at least partly carotenoid in character, while the remainder was considered to be possibly an oxidative decomposition product of original carotenoid pigment.

Resing[118] studied the chromatographic behavior of the pigment from clone PB 186 as compared to several other clones. It appeared that the pigment in PB 186 latex was not a single compound. The presence of carotenes was established, the main component being almost certainly beta carotene. In addition, the presence of a red epiphasic pigment was observed, while phytoxanthins were also found to be present, mainly in the esterified form. Chromatograms were prepared of pigments from other clones, and they showed essentially the same pattern as PB 186. In all cases, except PB 186, the amount of hypophasic pigment before saponification was negligible.

In an attempt to verify these results, obtained in the Far East, Verhaar[119] in Liberia repeated the partition test with a cold acetone extract of PB 186 crepe but was unable to obtain a colored hypophase, either before or after saponification of the extract residue. It therefore seems that either the cartenoids present in Hevea latex are all of the hydrocarbon type or external factors such as climate or soil type influence the composition, even in the same clone.

Kidder[120] obtained an absorption curve by subtracting a postulated absorption due to oxidation products and some background absorption. This derived curve had peaks at 438 and 465 millimicron and was similar in appearance to the curve for alpha carotene in ethyl alcohol, the only difference being that the pigment curve was shifted 7 to 10 millimicron toward shorter wavelengths. He therefore opined that the natural yellow coloring material in rubber is closely related to alpha carotene but may not be identical with it.

It is well known that carotenes are very susceptible to air oxidation and extraction at elevated temperatures might be the cause of structural changes. This was indeed indicated by a considerable difference in the absorption curve of the acetone extract after hot and cold extraction, as shown in Figure 4[119]. Using a War 4 crepe prepared by drying the milled sheet at room temperature (28–30° C), this crepe was extracted with acetone at room temperature until colorless. The absorption (curve A) is given in Figure 4. This curve is typical for a carotene compound showing a distinct maximum at 422 and 441 millimicron and indications for other maxima at 400 and 470 millimicron. When this same crepe was extracted for 22 hours at 50° C (as in the acetone extract test method) curve B (Figure 4) was obtained (concentrations are arbitrary). The distinct maximum at 441 millimicron has disappeared and there is considerably more absorption in the ultraviolet region. When absorption curves

are to be used as a means of identification for cartenoids in Hevea rubber, obviously, crepe extraction should be done at low temperatures.

Further analytical work by Verhaar[119] confirmed the presence of at least three carotenoids in Hevea rubber, different in chemical structure on the basis of their chromatographic behavior but very closely related as shown by their absorption spectra.

During processing, crepe is subjected to a temperature of about 37–40° C for drying and chances are that during this period oxidation products are formed of the parent carotene, originally present in the latex. It would therefore be of interest to extract the pigment(s) directly from the latex and compare the absorption curves. This operation was successfully carried out[119] and the absorp-

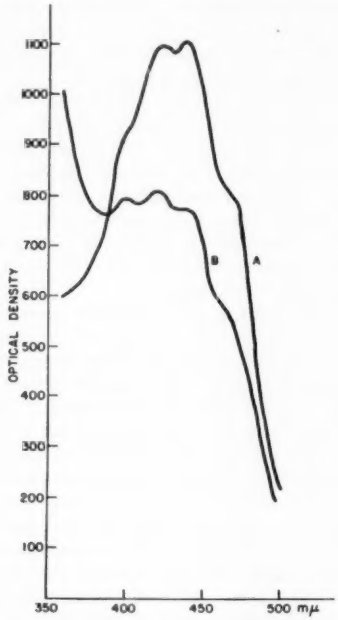

FIG. 4.—Absorption curves of acetone extract of crepe rubber. A, cold; B, hot.

tion curve for the pigment in benzene is given in Figure 5. It is obvious that absorption in the ultra violet is very low and that maxima at around 380 and 400 millimicron are absent. The benzene solution was further used for chromatographic analysis over a column of Florisil. The chromatogram consisted of one band which could not be separated into more zones of development.

It is therefore very probable that the yellow pigment as originally present in Hevea latex consists of only one carotene compound and that other compounds found on chromatographic analysis of crepe extracts are formed by oxidation of the parent carotene during processing, particularly drying.

The first practical method of determining yellow color in Hevea crepe or

latex film has been reported by Kidder[120]. The method consists of milling a sample until very thin and extracting it with acetone, as is done in the acetone extract method. Absorption of the extract is then determined in a spectrophotometer using the three different wavelengths of 360, 440 and 550 millimicron, respectively. The absorptivities are combined by an empirical equation:

$$\text{Color index} = a_{440} - 0.20a_{360} - 0.8a_{550}$$

to give a measure of the yellow coloring matter (C.I. = Colored Index). The test may be carried out even in the presence of considerable darkening of the sample due to oxidative processes. An analytical derivation by Verhaar[119]

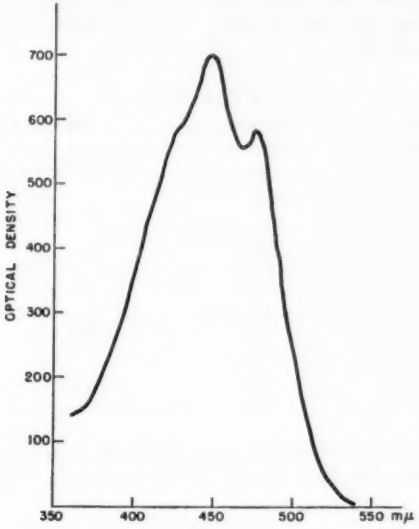

FIG. 5.—Absorption curve of yellow pigment present in Hevea latex.

using as a reference material colorless extracted crepe having a theoretical zero index resulted in the equation:

$$\text{Color index} = a_{440} - 0.19a_{360} - 0.81a_{550}$$

in very good agreement with the empirical formula of Kidder.

Using this method and "Carotene, 90% beta − 10% alpha" from Eastman Kodak as a reference substance, Verhaar[119] found the following equation for the carotenoid concentration of crepe rubber:

$$C = 0.006175/g \times d'_{440}$$

where d'_{440} = adjusted optical density of the acetone extract at 440 millimicron and g = weight of sample in grams. So, for instance, in a crepe sample weighing two grams and showing a d'_{440} of 500, the amount of carotenoid would be

1.54 mg/100g. This corresponds to a C.I. of 125, characteristic of an intensively yellow crepe. Eaton and Fullerton[116] found a carotenoid content of 2.0 mg/100 g in the first fraction of a fractionally coagulated crepe. This would correspond to a C.I. of 162.

The relation between carotenoid concentration and color index is given by:

$$C = 0.01235 \times \text{C.I.}$$

A normal range of carotenoid content in Hevea crepe would be 0.10 – 1.00 mg/100 g.

The method of Kidder has obvious uses in controlling the manufacture of pale crepes and for checking the yellow color content of films from latex concentrates. It was observed that crepes differ considerably in the amount of yellow color and that the color intensity was characteristic of the clonal origin. Typical examples are given in Table XI.

TABLE XI

Clone	Color index	Visual rating
BD 10	8	very light colored
TK 12	8	
BD 5	9	
AV 152	9	
PB 180	13	light colored
AV 50	24	
Tjir 16	24	
PB 183	26	yellow
AV 49	30	
Tjir 1	43	
PB 186	58	very yellow
War 4	60	

A classification system which will cover the whole range from white to highly yellow colored crepes has been suggested by Verhaar[119]. This classification is as follows:

Class	Color Index	Color quality	Visual appearance
IA	0– 5	very good	almost white
I	6–20	good	very pale yellow
II	21–40	medium	pale yellow
III	41–70	poor	yellow
IV	71 and higher	very poor	intense yellow

In this system class IA would include, chiefly, crepes which have been artificially decolorized.

It should be mentioned here that apart from being yellow due to the presence of carotenoids, Hevea rubber may also show a brown, grey or even black discoloration caused by the action of oxidizing enzymes and the formation of melanin-like substances[121]. These substances are insoluble in acetone, therefore this type of coloration is not measured in Kidder's method and does not contribute to the color index of a given crepe as expressed by that method. A direct relationship between visual appearance and color index therefore only holds true for crepes that are well preserved with sodium sulfite and do not show signs of oxidative discoloration. It should also be mentioned that sodium sul-

fite is often but erroneously referred to as a "bleaching" agent. Actually, apart from its preservative action, its further effect in crepe processing is the prevention of melanine formation (blackening), however, addition of sulfite does not decrease the color index and consequently does not lower the carotenoid content.

As far as the location of the yellow pigment in latex is concerned, Frey-Wyssling[122] found that in latexes of different origin there are present among the rubber particles another kind of globules which are distinctly bigger and consists of "resin". These globules (referred to as FW globules in this report) carry the yellow pigment and it was because of this that they were first detected in latex from trees which yielded a yellow latex. Later it was found that FW globules consist mostly of fat and fat-like substances and account for most of the acetone extract residue. It therefore falls in line that the fat soluble but not water soluble carotenes are located in these globules. In microscopic images of ammoniated field latex they can be detected, if the pigment concentration is sufficiently high, showing an average diameter of 1–3 micron.

With the discovery of FW globules in Hevea latex the picture is not yet complete. Research on unpreserved field latex revealed that it is not merely a dispersion of rubber particles in an aqueous serum but that it contains another dispersed phase: small, irregularly shaped, viscous, colloidal bodies. On batch centrifuging fresh, undiluted latex these bodies are collected at the bottom of the tube as a separate layer with a sharp boundary. The top layer was called the "white fraction" and the bottom layer the "yellow fraction" by de Hann-Homans and van Gils, who were the first observers of this phenomenon. Miss Homans made the first observations in 1941 but, because of the war, the work was not published until 1948[123,124,125126]. The most striking properties of these fractions are 1) The white fraction constitutes a much purer latex with a higher DRC. In spite of the higher DRC the white fraction is less viscous than the original latex. 2) The yellow fraction generally has a DRC of 8–15% and contains a considerable amount of non-rubbers. The viscosity is very high and tends to increase rapidly on standing. 3) Whereas the original latex coagulates spontaneously within about 8 hours, the white fraction may stay liquid for days. The yellow fraction, on the other hand, coagulates within a few hours.

The difference in composition is evident from the following table:

TABLE XII

PROPERTIES OF WHITE AND YELLOW FRACTION. VAN GILS[126]

	Original latex	White fraction	Yellow fraction
Weight ratio	100	76.3	23.7
Viscosity—cp	11.7	9.2	very high
DRC	34.8	43.7	9.0
TS	37.4	45.8	14.3
TS—DRC	2.6	2.1	5.3
Nitrogen	0.24	0.22	0.33
Ash	0.60	0.47	1.11
In the crepes prepared therefrom;			
Nitrogen	0.37	0.34	0.73
Ash	0.15	0.13	0.50
Acetone extract	2.42	2.10	6.99

There are wide variations in the appearance of the yellow fraction of the various latexes. Visually, it is not a homogeneous material, but appears to

consist of a light grey, pasty material with the yellow coloring matter distributed within it in a variety of forms. This color distribution depends, even for a given clonal latex, on the time of centrifuging and the preservative used. Observation of these phenomena in a large number of latexes, together with a microscopic study of the occurence and distribution of FW globules leads to the conclusion that the yellow color is not an intrinsic property of the viscous bodies, which were named "lutoids" (Latin: luteus = yellow) by de Haan-Homans and van Gils. As stated before, the yellow pigment (carotene) is located in the FW globules and the appearance of the yellow fraction therefore depends on the distribution of the FW globules, which are usually found irregularly scattered in the viscous bodies. Therefore the name "lutoid" did not seem very appropriate. High viscosity being a true characteristic of this material, Verhaar[121] proposed the name "viscoids" for these particles, a term that will be used in this report.

The general concept of the structure of fresh latex as derived from these recent experiments was further confirmed by Cook and Sekhar[127] who, by centrifuging at 59,000 g, obtained four fractions described as: 1) a thick cream of rubber particles, 2) a layer of orange yellow FW globules below the rubber, 3) clear serum and 4) a gelatinous grayish yellow viscoid fraction, with some rubber particles and FW globules trapped in the viscoid agglomerates.

The chemical structure of the viscoid was further investigated by Paton[128] who found evidence that there is an association between proteins and lipids. This complex has enzyme activity as shown by the rapid fall in pH which takes place on standing. The fall in pH of latex during the first few hours after tapping can also largely be attributed to changes taking place in the viscoid fraction. The affinity of the units making up the viscoids is increased by a fall in pH. This can be attributed to anion/lipid/protein association to give macromolecules which theory supposes depends upon the electrostatic forces between charges which are concentrated at a certain point in the constituent molecules.

The discovery of viscoids in Hevea latex has contributed greatly to a better understanding of latex and rubber processing. For instance, coagulation can now be described as follows. The process is characterized by a gradual increase in viscosity of the latex. Next step is the formation of a thin paste, gradually thickening and turning into a gelatinous mass until finally a solid coagulum is formed. If this process proceeds slowly enough it can be followed under the microscope. During the first stage the latex contains a large number of viscoids, varying in size and shape. In the course of a few hours several smaller viscoids unite to form larger conglomerates, thereby embedding a portion of the rubber particles. The latex remains quite liquid in this stage with a relatively low viscosity.

During the second stage the viscoid conglomerates continue to grow so that the microscopic image comes to resemble a deltoid landscape with wide branches of a river streaming along large islands between the banks. The "rivers" are still densely packed with a mass of free flowing rubber particles and the "islands" have nuclei of viscoids surrounded by areas of immobilized rubber particles. The latex is still liquid but gradually acquires a higher viscosity.

In the third stage the "rivers" are getting narrower and the intensity of the mass of free flowing rubber particles is gradually decreasing. The "islands" continue to grow by attaching more rubber particles and form connections between them so the landscape comes to resemble a hilly country with many lakes and small streams between the hills. In this stage the latex as a whole is no longer free flowing but has turned into a paste, although it is still easy to pen-

etrate with a glass rod. Ultimately the "rivers" and "lakes" dry up and the latex has turned into a coagulum. The phenomena described here are basically the same, whether coagulation is spontaneous or acid induced.

The process of fractional coagulation, as used in the manufacture of sole crepe, can also be explained on this basis. By adding acid to the non-diluted or slightly diluted latex (usually ¼ to ⅛ of the amount of acid required for total coagulation) the latex is brought into a state as described as the second stage. The viscoids act as nuclei around which a portion of the rubber particles (presumably those having the lowest colloidal stability) are bound, thus losing their Brownian movement just as does a solute in the process of crystallization. These rubber-viscoid complexes clot together when the latex is stirred and are removed by screening. Since the carotene carrying FW globules are mainly embedded in the viscoid agglomerates they are removed from the latex along with the pre-coagulum. Removal of viscoids and FW globules, yielding a purer and light colored crepe from the remaining fraction, is therefore the essential feature in precoagulation.

Initally it was thought that ammoniation of Hevea latex led to an almost complete dissolution of the viscoids but further studies by van Gils[129,130] and Verhaar[121,131] showed that addition of ammonia profoundly changes the struc-

TABLE XIII

NH_3, %	Av. size of viscoids, micron
0.000	30–200
0.025	15–100
0.050	5– 25
0.075	3– 15
0.100	3– 5
0.150	3– 5

TABLE XIV

Sulfide, %	Av. size of viscoids, micron
0.00	70–150
0.02	50–100
0.04	30– 70
0.06	25– 50
0.08	20– 50
0.10	10– 50
0.15	10– 30
0.20	5– 30
0.25	5– 30
0.30	5– 30

ture of latex by complete disintegration of the seemingly complex viscoids into units somewhat bigger than rubber particles. It was further found that increasing the ammonia content by very small increments brought about a rapid breakdown in average size of viscoids as illustrated in Table XIII. When the viscosities of these latexes are plotted in relation to preservative concentration the curves show a fast drop in viscosity by addition of ammonia up to about 0.05 per cent, followed by a break in the curve at that point and a slightly decreasing viscosity at higher ammonia concentrations[131,130].

In comparing viscosity-preservative concentration curves of ammoniated and sodium sulfite treated latexes characteristic differences are, first, that the curves for sulfited latex are smooth and do not show a breaking point, second, that the minimum viscosity is reached at a higher level, and third that in sulfited latexes no relationship can be found between DRC and viscosity. Microscopic observations showed that sulfite tends to disintegrate the viscoid complex only partially[121]. An estimate of the average particle size in sulfited latex is given in Table XIV. In both ammoniated and sulfited latex it therefore seems that the course of viscosity is related to the behavior of the viscoids and this may even be generalized by stating that any change in the colloidal structure of Hevea latex bringing about an increase in viscosity (conglomeration of viscoids)

causes pre-coagulation and any change that is accompanied by a decrease in viscosity (disintegration of viscoids) tends to stabilize the latex.

The principle of controlled pre-coagulation is used in processes where the pH of the latex is adjusted between 6 and 8, usually by addition of a small amount of ammonia. Under this condition the latex can be used either for the preparation of a "white fraction" cream[132] or for the preparation of a pale crepe, whereby partial acid coagulation is replaced by spontaneous coagulation of the yellow fraction, with the white fraction remaining liquid at the same time[133].

Dilution of unpreserved latex with pure water has a profound influence on both the viscosity and the viscoid structure. It appears that addition of water up to 15 to 20 per cent causes a viscosity increase followed by a gradual decrease at higher dilutions[130,131]. Following the process of dilution microscopically it could be observed that the increase in viscosity coincided with the formation of bigger viscoid complexes, this phenomenon showing a striking resemblance to the first stage of acid or spontaneous coagulation. It therefore seems that water alone in concentrations up to 20 per cent is able to cause a change in the colloidal structure of latex which brings the latex into a stage of precoagulation. This explains why, in estate practice, rain dilution of field latex often causes trouble in handling the latex due to a tendency to precoagulate in the field.

The formation of bigger viscoid complexes may be ascribed to two factors, clotting and swelling. The former is caused by a decrease of the repulsive electrical forces and the latter by water transport from the serum into the viscoids as the result of a lowering of the ionic strength of the serum.

In explanation of these phenomena it may be considered that water in Hevea latex is present in three different stages: 1) as the vehicle for the suspended rubber particles, viscoids and FW globules, at the same time acting as solvent for salts and other non-rubber constituents that are in true solution; 2) as a hydration shell around each individual rubber particle in which the water molecules are arranged in a semi-crystalline structure[95], and 3) as the main constituent of the viscoids which have been reported by Homans and van Gils[124] to contain 80–85% water. Further, Ruinen[134] found that the viscoids are composed of a gelatinous central body and an enveloping membrane. In this system viscoids and serum are in osmotic equilibrium but when the latex is diluted this equilibrium is disturbed by a decrease in the ionic strength of the serum. To restore it the viscoids will take up more water and thereby swell. The formation of these bigger viscoids accounts for the initial increase in viscosity of water diluted latex. This view is supported by the fact that latex can be diluted without any apparent change in the viscoids if a 0.1 *N* solution of a salt such as NaCl or KCl is used[135,136,137]. In that case the osmotic equilibrium is maintained.

On addition of increasing amounts of water there apparently comes a point where the complexes have reached their maximum size, coinciding with the peak in the viscosity curve. By addition of still more water it is assumed that the structure of the viscoid complexes is destroyed and the individual viscoids cease to exist because the enveloping membranes burst and the gelatinous central bodies are dispersed in the serum and mix homogeneously, although many constituents may still occur in a macromolecular (colloidal) state. This phenomenon is then accompanied by a steep drop in viscosity of the diluted latex.

The relationship between dilution and viscosity described here for fresh, unpreserved latex does not hold true for centrifugal concentrate. In that case the curve purely describes the effect of dilution on the viscosity of a non-New-

tonian liquid. This type of curve is also obtained when ammoniated field latex is diluted, indicating that addition of ammonia has stabilized the viscoid phase to such an extent that they neither swell nor agglomerate[119].

The discovery of viscoids in Hevea latex has also led to investigations and speculations on their location in the tree, their teleology and possible role in the formation of rubber in the plant. Verhaar[119] considers that the material used by the rubber tree to build up the adsorption shell around the rubber particles and the viscoids are essentially of the same composition (proteins, phospholipids). From this point of view, this material is produced by the rubber tree for the purpose of creating colloidal stability for the (hydrophobic) rubber particles. The viscoids, present as a sepatare phase, are then considered surplus material and non-essential in the end product from a biochemical standpoint. Speculating on the reason for the presence of this surplus material it is obvious that the amount of material needed for the formation of a protective adsorption shell is greatly dependent on the ultimate size of the rubber particle. Recent investigations have shown that there is a wide spread in particle size for various clones and under varying conditions of tapping (see Section II).

Now it seems as if nature has provided the Hevea tree with a biochemical system capable of producing an excess of protective material, so that, regardless of the amount needed for the formation of the adsorption shell, there will always be enough available to ensure colloidal stability of the latex produced.

Schweizer[138] proposed that the viscoids originate partly if not wholly from the sieve tubes. In that case the viscoid material can only be considered as a "foreign body" or contamination of the latex proper. However, Ruinen and de Haan-Homans[139,140] have refuted this hypothesis. By anatomical examination it was found that in normal tapping not more than 10 per cent of the functioning sieve tubes are cut and that latexes collected separately at various depths show the normal microscopic image with regard to viscoids and a content of 20–30 per cent viscoids in the centrifuged latex. Collected evidence from these and other findings therefore led to the conclusion that viscoids do no enter the latex as a product of the sieve tubes, but occur in the latex vessels.

Schoon and Phoa[20] found evidence that the rubber particles as ultimately found in latex are built up from much smaller (primary) particles and consider that polymerization of rubber could take place inside a vacuole as present in viscoids. They believe it possible that the rubber particle is formed inside the viscoid vacuole and that the viscoids are the "polymerization vessels", used by the tree to synthesize the rubber. After the vacuole is filled with primary particles the so formed secondary particle is surrounded by a skin of protoplasm—the original viscoid membranes. After tapping, one should find in the latex: 1) older, already filled viscoids or secondary rubber particles, and 2) freshly formed viscoids, not yet filled with rubber and centrifugable as viscoid fraction from the latex. However, much work remains to be done to futher evaluate this and previous speculations. The parts of the plant tissue from which viscoids and rubber particles actually originate are still not known, but according to the most recent investigations the possible dual role of viscoids in latex formation, as discussed, is not contrary to the occurrence of these bodies in the latex vessels.

In conclusion, it is clear that over the last twenty years great strides have been made towards a better understanding of fundamental processes occurring in the rubber tree and that new vistas have been opened for continued and fruitful research.

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THE PRESERVATION AND CONCENTRATION OF HEVEA LATEX

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I. INTRODUCTION

Some twenty years ago the author stated[1] that, "in the simplest form latex at the time of tapping may be defined as an aqueous buffered neutral system containing water-soluble crystalloids and fatty acid esters, in which small rubber particles are dispersed by means of a vegetable protein—said protein operating on the basic side of its iso-electric point". Since that time we have had more information about the crystalloids and about the fatty acid esters but essentially the definition still holds.

He also went on to say, "it is desired to use this word 'preservation' in its broad sense, that is, the maintenance or improvement of the system in all of its aspects . . . by the term preservation we are including not only methods that prevent bacterial action or guard against outside infection, but also methods which involve the use of actual stabilizers for the improvement of mechanical stability. In the first case we deal with disturbances that occur within the material itself. In the second case we deal with disturbances that occur either within or without. It is essential that a preserving substance should prevent bacterial action or fermentation of the protein or like materials. It is also es-

sential to maintain the original state of dispersion when any serious stress is put upon it". In this article we will attempt to outline the more recent, broader aspects of preservation which are essential to the commercial use of natural latex.

II. SIGNIFICANCE OF TOTAL SOLIDS

One of the most important variables in latex preservation is the total solids content of the dispersion. The data of Arisz[2] indicated that the nitrogen content of a freshly tapped latex is nearly constant when based on the whole latex and not a function of the rubber solids. McGavack and Rhines[3] checked this fact and in addition found that not only the protein but also the ash content is independent of the T.S. value. Freshly tapped whole latex covering a total solids range from 24 to 50 per cent had a nearly constant nitrogen content to 0.25 per cent and ash content of 0.50 per cent. These facts should be weighed in studies invloving preservation and concentration.

The fact that ash and nitrogen are nearly constant for the whole latex means that a low solids latex has a high protein and ash based on the rubber content. If the latex is concentrated by evaporation these factors remain high but if concentration is accomplished by separation of serum as by centrifugation then the sh and protein based on the rubber content will be lowered by the amount

TABLE I

SIGNIFICANCE OF TOTAL SOLIDS IN LATEX PRESERVATION

			Amount preservative per 100 parts whole latex			
	Composition (%)		Ammonia (no interaction)	Formaldehyde (interaction)		
Latex	T.S.	Water	Total	Non-rubber	Water	Total
1.	30	70	1.40	0.15	0.049	0.199
2.	40	60	1.20	0.15	0.042	0.192
Ratio 30/40% total solids			1.16			1.03

removed in the serum. Preservatives that do not interact, such as ammonia and boric acid, should be added as a percentage of the water content of the latex, while preservatives that do interact, for example formaldehyde and ethylene diamine tetracetic acid should be added partly as a percentage of the water content and partly as a percentage of the ash or protein content of the latex. Table I illustrates these facts for ammonia and formaldehyde.

These facts indicate, both from a cost and a quality consideration, the importance in any study of the preservation formula of the total solids value, which varies widely with clone, method of tapping and age of rubber.

The relation between total solids and nitrogen content of latex also has an enormous effect upon the uniformity of natural crude rubber, It is the source of some variation in the cure and to some extent enters into the normal aging of the rubber. In articles made from latex we also have the same effect in the final vulcanizate. For this reason it is preferable for a plantation manager to supervise the collection of his latex so as to have as uniform starting total solids of the latex in his process as possible. It is well known that different clones, different methods of tapping and the age of the rubber have a good deal to do with the total solids content.

III. PRESERVATION

A. PREEMINENCE OF AMMONIA

To date ammonia has been the most widely used preservative for latex. In fact, even today over 95 per cent of all the latex imported contains some ammonia. The reason for the use of this material is not hard to understand. Let us go back to our original definition. There it will be noted that in a simple latex system the rubber particles are kept dispersed by means of a protein and that the dispersion has a neutral reaction and contains salts. These are ideal conditions under which proteins if properly inoculated will decompose, and the tapping system, no matter in what manner it may be operated, opens up golden opportunities for infection of the latex. If the proper measure is not taken the bacterial activity becomes so rapid that in the course of about six hours from the time of tapping latex will spontaneously coagulate.

One way to prevent the bacterial putrefaction of a protein is to change its pH by making it more acid or more alkaline. As our definition tells us, the protecting protein found in latex is on the basic side of its iso-electric point. We would therefore surmise that the easiest way to prevent bacterial activity by change of pH would be to make the system more alkaline; that is why ammonia prevents putrefaction. With ammonia a pH of 10.2 is sufficient to give latex good preservation.

In addition to this factor remember that our freshly tapped latex contains fatty acid esters. It has been shown that the fatty acid radicals of these esters are, in the main, those of oleic, linoleic and stearic acids[4]. When ammonia or any other base is added to latex, not only do we raise the pH of the system but we also tend to hydrolyze these fatty acid esters and in the process form soaps. These soaps, in turn, act as stabilizing bodies for the dispersed system. For example, the mechanical stability of latex as measured by any of the known methods is not great when freshly tapped but if ammonia is added to the system in sufficient amounts the mechanical stability gradually rises from day to day until after a period of approximately one month it reaches a maximum at a level considerably higher than its original stability. In other words, ammonia, in sufficient amount, is an ideal preservative because it not only prevents bacterial action but also forms stabilizing soaps from the fatty acid esters naturally occuring in the latex.

Ammonia well embodies the two actions mentioned above as needed for complete preservation, and in considering any other methods these two aims must always be clearly kept in mind—prevention of bacterial infection and the maintenance of stable dispersions. No doubt the long line of preservatives tried have in many instances been found wanting due to the fact that only one side of this dual preservative function was considered.

The disadvantages if ammonia are that it is relatively expensive and is a complete loss when latex is sold on either the total solids (TS) or dry rubber content (DRC) basis; it has a disagreeable odor in the factory; it is a health hazard, particularly for women workers; it is inflammable under limited conditions—all characteristics to be avoided if possible. Nevertheless, due to its great usefulness as suggested above it is still being employed in some amount with almost all latex. As a single preservative it should be used at a concentration of a little over two per cent on the water phase of the concentrate. With that amount, without other chemicals and using good sanitary conditions, the latex should have a useful life of 18 months without any serious deterioration. At the two per cent level the latex is brought to a pH where oxidation[5] is at the highest rate.

This is one of the reasons full tank capacity and low temperature storage facilities should be used in all handling of latex where ammonia is the sole preservative.

B. REQUIREMENTS FOR PRESERVATION

During the past twenty years many papers have appeared relating to the preservation of latex. Hastings[6] emphasized the cleanliness in ships' holds. Ascoli[7] gave a pen sketch of latex collection and preservation of the latex on the estate and indicated the necessity of consistent procedure. However it was not until the Second World War arrived that there was a united effort by all to put in print the best known methods for the preservation and storage of latex. We were cut off from our supplies of new latex and hence needed to muster all the technique available to protect what meager supplies we had. At the request of the Rubber Section of the War Production Board the author compiled such information, gleaned in the most part from unpublished records of various rubber companies. As a result, two short publications[8,9] were released describing quite clearly the best thinking as to how latex should be preserved and stored in such a way as to maintain its usefulness.

Eight different requirements were given for preserving and storing latex. These were:

a. It should be free from bacteria.
b. It should have a sufficiently high pH level depending upon the type of latex.
c. It should be maintained at uniform total solids.
d. Temperature should be uniform and properly regulated.
e. Storage vessels should have smooth side walls and should be properly sterilized.
f. It should have minimum exposure to oxygen.
g. It should not be exposed to either direct or indirect light.
h. It should have low KOH number.

All of these criteria are discussed more fully in the original paper and are generally understood. One of them—point c—has already been touched on in the present paper, giving another slant to the importance of uniform total solids. All of them are still essential today. In several instances however modifications and adjustments are called for. These will be outlined in the present paper and in addition several new criteria will be added.

The first factor listed—freedom from bacteria—is the most important consideration in the entire latex field. Unless properly accomplished, all other factors become meaningless. Ammonia is a mild bactericide and in the case of latex a high concentration—over two per cent on the water—gives the best and most consistent results. Lower amounts have been used commercially but with the risk of a deteriorated commodity if some adverse, unforseen circumstances arise. The fact that it is volatile and is eliminated from the final rubber product is a big advantage. Also the fact that it hydrolyzes the fatty acid esters, with the subsequent formation of soaps imparting increased stability, has always been a point in its favor and is still a large factor in its not having been completely replaced. It is believed that ammonia in some amount will be with us in latex preservation for a long time.

Mention should be made of heat sterilization methods. Among others, Spence[10] wished to employ this method along with a phosphate buffer.

Stewart[11] wished to use the heat method but at a little lower temperature. This is the old milk therapy and is good enough for short periods and where all equipment is meticulously sterilized and kept so. To be useful for latex it would be necessary to add artificial cooling. Beyond the point of keeping all equipment as scrupulously clean as possible, heat sterilization methods are not sufficient for practical latex preservation.

C. BACTERIA INVOLVED AND WAYS FOR FINDING THEM

In unpublished work of Rhines[12] in Sumatra in the late thirties the fundamentals of modern latex preservation were laid. A keen bacteriologist, he attacked the problem at its roots and found that latex kept with moderate concentrations of ammonia for long periods of time developed bacteria that caused severe damage and once developed could not be eliminated by the addition of very high amounts of ammonia. These bacteria removed from ammonia died and were only virulent and destructive in the presence of the free material itself. They are very difficult to detect and special and somewhat laborious procedures have to be used to quantitativly determine their presence. The answer at that time was to improve housecleaning methods and raise the ammonia concentration level in the latex shipments.

An interesting discussion of bacteria in latex obtained in the Belgian Congo is given by Simonart[13]. Great numbers of Achromobachter bacteria were found to be present.

The general procedures and methods for determining and controlling these highly ammonia-resistant bacteria are given by Rhines and McGavack[14]. Their article gives specific details and the proper bacteriological technique for determining such bacteria in latex. More recently Tysum has reviewed the microflora of Hevea latex in several interesting papers[83,84,85]. These papers give specific instructions on determination of the usual bacteria in latex, but for the virulent ammonia-resistant type the method of Rhines[14] is much to be preferred. The ready disclosure of the presence of bacteria in latex reemphasizes the principle that to maintain high quality material, all equipment that comes in contact with the latex must be cleaned scrupulously with steam or a good sterilizing agent such as lysol or formaldehyde.

D. SIGNIFICANCE OF CHLORPICRIN

For salvage purposes, it has always been desirable to have a disinfectant that would kill off immediately any bacterial invasion that has developed from highly ammonia-resistant strains. There are two chemicals that will do this job. Formaldehyde can be added to ammoniated latex and will eliminate very quickly any inherent infection. However, it also reacts with the ammonia and hence will cause coagulation unless a very powerful stabilizer is added. Also, it is not too desirable to have any form of hexamethylenetetramine as an ingredient in compounding latex. The author has proposed chlorpicrin[15] to do this job. This chemical gives an excellent account of itself and will completely sterilize a highly infected latex in a matter of a few hours with an amount less than 0.1 pound on one hundred pounds of latex. Such procedure is only makeshift and the conditions calling for its use should not be allowed to exist. Chlorpicrin on long standing in an ammoniacal solution hydrolyzes slowly. For this reason, although good for a quick disinfection, chlorpicrin cannot be classified as a long time preservative. Resing[16] proposes a method for preserving latex for short

periods of time. He uses dehydroacetic acid with ethylenediaminetetraacetic acid (Sequestrene) or as an alternate the combination of formaldehyde and phosphates.

E. AMMONIA AND FORMALDEHYDE

There is one ammonia combination with another chemical that deserves mention. That is the use of formaldehyde with ammonia. This combination developed in the early thirties by the author[29] has been in continuous commercial use for the last twenty five years. The method consists in treating the latex at the collecting station as soon as possible after tapping with 0.15 to 0.20 parts of formaldehyde for every one hundred parts of latex. The latex is then brought into the factory and allowed to stand from 15 to 30 hours after which time a very small amount of ammonia is added to bring the pH up to a little above 6. If a concentrate is to be made the latex may then be centrifuged. At the end of the centrifugal operation ammonia is added to the concentrate up to about two per cent on the water. The reason why this latex has been so popular with its users, despite the fact that it has characteristics somewhat different from the usual ammonia centrifuged concentrate, is that (a) it is very uniform from shipment to shipment, (b) has an extra long storage life without deterioration, (c) a high mechanical stability, and (d) greater resistance against freezing temperatures. This latex has been sold at a premium over the usual centrifuged ammonia concentrates mainly due to its different and exceptional qualities.

The reasons for the unusual and interesting properties of this particular concentrate deserve consideration. We believe the answers are simple and straightforward. The addition of a very small amount of formaldehyde to latex kills almost at once—within fifteen minutes—all the bacteria present in the tapped latex. This killing is accomplished in the first few minutes after the formaldehyde is added. The time lapse before the addition of ammonia allows the small amount of formaldehyde present to react with the proteins of the latex forming a formaldehyde-protein complex that does not break up under severe heating. This reaction is not too rapid but is essentially completed before the small amount of ammonia is added to bring the pH of the dispersion back to the neutral point. The drop in the pH upon the addition of formaldehyde is caused by the release of free carboxyl groups in the protein. Furthermore, it is this formaldehyde-protein complex that enhances the stability of the latex and lowers the freezing point. The lower pH completely eliminates any oxidation and leaves a well preserved protein in the finished concentrate. More complete information on the formaldehyde-ammonia combination was published in 1946[8,9].

A more recent version of the formaldehyde alkali treatment has been proposed by Ten Broek[30,31] in which he suggests the addition of small amounts of formaldehyde in the presence of 0.1 to 0.4 per cent of a base such as sodium or potassium hydroxide. Such preservation is intended for a short period of time—just enough to allow precipitation of the calcium and magnesium ions in the form of difficultly soluble hydroxides which are eliminated from the system either by settling or by desludging operations. This procedure has merit in that it allows bacteria present to be killed and also furnishes an alternate method for removing some of the metal ingredients in the form of sludge. No quantitative data is given in the patents to show just how much of the sludge can be removed. It is noted that after the concentrate is prepared ammonia may be added, a fact which makes good sense as ammonia, weight for weight, has better preserving value than sodium hydroxide. It is believed that on the alkaline side the re-

action rate between protein and formaldehyde is slower than on the acid side of the neutral point and hence there may be more free formaldehyde left in the dispersion than in the procedure described above using ammonia and formaldehyde Furthermore, it is questionable whether or not as much of the formaldehyde-protein complex is formed which, if true, would indicate a less mechanicallly stable latex. There are also disadvantages from residues when fixed alkalis are employed. For preliminary concentration of latex, however, such a method could be useful.

Another method of preserving is that of Rhines[32] which consists in treating latex first with formaldehyde and then removing the free carbon dioxide before any additional alkali is added. This removal can easily be accomplished by blowing air through the latex or by using a vacuum or by agitating and blowing air or nitrogen across the surface of the latex. This method permits the preparation of a concentrate which has a 0.2 less KOH number than a similar latex not so treated. Unfortunately the method is more expensive than present methods.

F. AMMONIA AND OTHER CHEMICALS

During the last twenty years continous search has been made for incorporating other materials with ammonia in order to eliminate some of the undesirable features of ammonia preservation alone. Albion[17,18] suggested small amounts of tetrahydronaphthalene with hydrogenated phenol. The author[19] proposed small amounts of alkyl mercury chloride and other mercury esters. Cake and McColm[20] offered arsenic trioxide. Stewart put forward acetaldehyde and ammonia[21]; quinoline in a medium having a pH 9.8 to 10.0[22]; nitro phenols, nitro benzoic acid and other nitro compounds[23]; amino phenol[24], and an alkali zincate[25]. Bevilacqua suggested the use of morpholine and formaldehyde[26] as well as methyl cellulose[27]. Rhines and Linscott[28] also show good preservation by the use of morpholine and formaldehyde. All of these materials were undoubtedly helpful in preserving latex but none were good enough to allow the ammonia content to be greatly lowered and still maintain good preservation for lengthy periods.

G. SODIUM PENTACHLOROPHENATE

Carswell[33] introduced sodium pentachlorophenate claiming preservation of latex with the use of this substance and a minimum amount of ammonia. His findings and predictions have produced positive and material results. This chemical is extremely poisonous and for this reason has been given very extensive clinical examination. Tests[34] carried out at the Fifth Avenue Flower Hospital New York showed that solutions of as little as one half of one per cent painted on the skin of rabbits caused not only a severe rash but also resulted in accumulation of the chemical in the liver of the animal. With lower concentrations, less harmful results were noted. The net result of this work and tests made at other institutions seemed to indicate at least concentrations of 0.05 per cent or lower would cause no difficulty. Even with higher concentrations no difficulty has been reported[16] and none would be expected, provided the products made from this latex were thoroughly washed during or after processing.

With smaller amounts more ammonia has to be used, but even so this chemical has found satisfactory use allowing considerable reduction in the ammonia content. It is the thought of the author except in very exceptional cases the

limits of 0.3 to 0.75 per cent proposed by the inventor are too high for safe usage and that users would be wise to know the concentration utilized in any particular latex. It is of interest to know that there have been several methods worked out recently to quantitatively determine the amount of sodium pentachlorophenate in latex. These methods are expected to be published in the near future.

Another interesting fact that has developed with the use of sodium pentachlorophenate is that small concentrations—0.05 per cent or below—added to the soil of young rubber seedlings is not harmful. It may give a positive small growth response. In other words, latex serum containing small amounts of this chemical can be broadcast on and around rubber plantings without any fear. However, such serum should not be allowed to be introduced into streams or rivers. It is possible in the future some other similar chlorinated phenol may supplant sodium pentachlorophenate for latex preservation but as of today this chemical has a very definite use.

H. MODERN METHODS

Quite recently, Philpott[35] published a very interesting review of natural latex preservatives currently in commercial use. Along with sodium pentachlorophenate, discussed above, he has listed three other chemicals or combinations, all of which contain approximately 0.2 per cent of ammonia. These other three are: zinc dimethyl dithiocarbamate, patented by Townsend[36]; an aminophenol, suggested by Resing[37] and by Stewart[24] in conjunction with ethylenediamine tetraacetic acid suggested by Rhines[38]; and boric acid, recommended by the Rubber Research Institute of Malaya.

Philpott lists the objections to complete preservation by ammonia alone and goes on to state that two or three of these preservatives "have recently been subjected to evaluation trials by latex users. One result of these trials is that latex producers are now offering 60.0 per cent centrifuged concentrate preserved with several novel preservative combinations". Then follows a review of the four combinations mentioned above. While the author is in agreement with most of the statements made in the article, there are a few which need further clarification.

Philpott notes: "A possible drawback to latex 3 (amino phenol and ethylenediaminetetraacetic acid) is that its films discolor severely on aging". It should be pointed out that a very small amount of zinc oxide added while compounding or before drying the film would eliminate all such discoloration. It is believed from considerable experience that the Rhines method[38] will be a great help in commercially selling large quanities of low ammonia latex, either centrifuged or creamed. There are a number of materials, especially chlorinated phenols, that dovetail with ethylenediaminetetraacetic acid to produce highly desirable concentrates. Remember that bacteria, like humans, cannot live without heavy metals and this chelating agent removes them from the active latex system.

Zinc dimethyl dithiocarbamate also holds considerable promise. We know that this has already found some commercial use and it is believed that such use will continue. As for boric acid, the amount added is against its use although not prohibitive. The ability boric acid has to stand up against destructive ammonia-resistant bacteria is not yet completely proven. Boric acid is a good chemical to have around latex. It is clean, non-toxic and in sufficient amounts

does the job with most latex concentrates. The high KOH number from its use is to be expected on account of the acidic nature of the chemical itself. Like all new methods there will have to be some adjustment in compounding to use boric acid preserved latex.

I. METHODS FOR FOLLOWING LATEX DETERIORATION

There are a number of ways of following latex deterioration. These may be listed as follows:

(a) The nose method, which requires only a sensitive nose. When available this is an excellent method and detects putrefactive changes rather readily;
(b) The oxidation method of McGavack, Bevilacqua and Ellis[39] which is long and tedious to apply but gives quantitative results;
(c) The KOH number of Jordan[40], which is quick and very definite and especially useful in long storage problems and in general compounding;
(d) The volatile fatty acid method of Philpott and Sekar[41], which is very valuable and especially useful in processing latex in the estate factory.

These four aids are quite sufficient along with the other usual latex tests to predict and maintain the proper sterility of natural rubber latex. One final important warning—apply the preservative, whatever it is, as soon after tapping as possible.

IV. CONCENTRATION OF LATEX

Natural latex as collected in the usual manner may have a total solids concentration ranging from 25 to 45 per cent. With few exceptions, latex manufacturing processes need higher concentrations and less non-rubber content in order to make their process practical. For this reason, methods had to be devised for concentrating and purifying latex. Also, it is expensive to carry water over long distances and this works to the disadvantage of natural latex as opposed to the use of synthetic latex. In other words, there is considerable urgency in economic and useful methods for concentration. The days when normal latex could be shipped to advantage have disappeared since the late thirties; all latex must now be concentrated. Satisfactory practical methods are available to do this job by centrifuging, by electrodecantation, by evaporation or by creaming. Other methods have been proposed and operated on a small scale but as of now latex is processed by one of the above methods.

A. CENTRIFUGING

Centrifugal methods were probably the first ones to be tried, emulating to some extent the milk industry. However, the machines built to separate milk were unable to cope with the smaller sized particles of latex. The separator companies went to work to develop faster, larger and especially equipped machines to do this job. The mechanical separation of latex was just getting to be a large business in 1936. Today, machines are operating that will produce six to eight times as large a volume of a concentrate as was done twenty five years ago. These highly successful developments have mainly been carried on by several large separator companies that had the proper facilities for experimentation.

The improvements did not come all at once as they involved considerable practical and engineering skill to bring them about. It meant testing new construction designs, new construction materials, faster centrifugal speeds, various ratios between speed of rotation and diameter of bowls. The range of particle size made the problem more difficult. There were no new principles to discover but the determination of the best application of those already known was involved.

In addition to larger machines developed there are other improvements such as those suggested by Nyrop[42] and Aktiebolaget Separator[43] for the elimination of sludge and dirt during operation. If these suggestions work out in practice they will be of considerable value to the user resulting in reduced processing cost. Capital cost would be reduced by the use of fewer spare machines.

The mechanical process of centrifuging has many advantages. In the first place, it means that today's latex will have to be completely concentrated within twenty four hours after receipt at the factory. From a business angle, this is highly important in that cash is received for the crop that much sooner. This is the big contrast between centrifuging chemically and creaming. There is, however, a risk factor. In the case of a breakdown, and there are insufficient spare machines, the latex cannot be held over the twenty four hour period without giving it further and adequate preservation, a fact which changes the characteristics and the quality of the product. This process also requires less preservative chemicals prior to concentration, which is a big saving to the manufacturer. It also allows the serum portion to be processed not too long after tapping thus enabling the preparation of a better off-grade with less cost. The point to be made here is that any latex, serum or whole, when being transformed into dry rubber is better accomplished when that serum is treated as soon as possible after the tapping date. This is due, in the case of an ammonia preserved latex, to the continuous formation of soaps from the fatty acid esters in the latex after the addition of a base. Too much base is not helpful in forming crude rubber from latex. Further this process enables the same daily output of latex to be processed with less working and storage space than is the case with creaming.

The biggest handicap centrifuging has when compared with creaming is that for a practical operation as high a recovery of dry rubber in the concentrate cannot be made. In a commercial operation an average of 90 per cent is above normal for the centrifuged product while 93 per cent recovery is very easily accomplished in a modern cream factory. This is a serious disadvantage but as stated above it is partially overcome by the fact that the serum of the centrifuged concentrate is easier and more economically worked up than the serum of a creaming operation. A happy combination is to operate both processes in the same general locality so that if difficulties occur temporarily in one the other method is available.

It was noted when discussing preservation that the methods used to preserve the latex were also designed to help remove more of the mineral matter of the latex[30,31]. It is believed in the future desludging methods will be used prior to centrifugal concentration. This will give longer runs in the centrifuge and hence save much time which is highly important in such operation. Such a process dovetails quite readily with the use of ammonia in the early stages of concentration as it allows the quick removal of phosphates and magnesium to a large extent.

Today, most latex centrifugal concentrates guarantee a dry rubber content of at least 60 per cent and generally come into the market having a total solids content of nearly 62 per cent.

B. CHEMICAL CREAMING

The intriguing invention of Traube[44] that latex can be concentrated by a vegetable mucilage has led to many experimental investigations of introducing colloids into latex. Here a lone wolf can easily try his hand and does not need a corps of engineers to conjure up a machine that would suitably apply all the right forces at the right time to do the job. All you need is a chemical, a test tube and a small amount of latex and you are in business. Hence, this field of adventure flourished and we have the record of many successes. Let us call the roll of creaming agents that have been disclosed during the past 25 years. D'Angremond and Sekar[46] have used ripe seed of arenga pinnata; Cherian[47] and Shanker[45] used tamarind seed powder; Vergese[49] coral wood tree seeds; Hauser and Dewey[50] and Mason[51] locust bean gum; Lumsdale[52] amorphallus; Rumbold[53] monoesters of polyglycols with long chain fatty acids; Mack[54] cellulose acetate dicarboxylates; Schmidt[55] introduced dibasic sodium phosphate with alginate; Vester[56] applied various colloids; Freeman[57] used aluminum cellulose glycollate. Here is quite a list of materials that will actually cream rubber latex that can be added to those previously disclosed. The two cellulose derivatives should be kept in mind as some day derivatives such as these with slight modifications could be a real find in latex creaming.

In generalizing about creaming agents, Philpott[58] stated that alginate[59] seems to be generally preferred. The author believes this is true. Certainly, all the big commercial creaming operations are carried out with alginate, generally the ammonium salt. This is really an ideal chemical and has been developed in very usable physical characteristics by several manufacturers. Alginic acid can be prepared in a very pure commercial form from cheap sources and its ammonium salt is readily soluble up to five or six per cent. Under heating, the ammonia is released just as is the case of an ammonium fatty acid, leaving an almost water-insoluble residue. The amount necessary to accomplish good creaming is very small, ranging from 0.07 to 0.12 part of material on an hundred parts of water, depending upon the condition of the alginate and the type of creaming desired.

Alginate is to creaming what Captax is to vulcanization. Because alginate is such a definite chemical and is slow in changing its physical characteristics, creaming with this chemical has become a very exact art. In other words, you can predict what kind of creaming will result knowing the amounf to the creaming agent, concentration of the latex, temperature of the latex and the time involved. If the results do not come out as expected you know that all of the proper conditions have not been fulfilled; some error in compounding had been made. This allows for easy correction and proper changes when such variations are discovered.

The mechanism of creaming is tied up with the condition of the surface around the rubber particle. In general, the creaming agent used changes the surface charges of these particles such that instead of the particles repelling each other they attract one another so that large aggregates are formed. This favors faster rising of the particles. Alginate in small amounts does this quite readily without allowing coalescence. There are special aids which further hasten the speed of creaming such as the ammonium fatty acid soaps proposed by the author[60] many years ago and still used with success, and a more recent one, a substituted phenol, suggested by Van Dalfsen[61] about which at present there is little information. The idea behind these aids is that you need a mild dispersing agent at the same time you are adding the agglutinating material in order to

keep the viscosity more uniform, thus allowing the aggregated particles to move more rapidly.

As stated when discussing centrifuging, creaming is a longer operation than centrifuging. This does not necessarily mean that centrifuging is more economical. Far from it! Actually, the capital needed for a commercial creaming setup is less expensive than that required to concentrate the same quantity of latex produced in about a month. Also, the upkeep of a creaming plant is not as great as a corresponding centrifuging plant. There are very few published data making this comparison but the statements made here would be hard to question. This takes into account all the necessary compounding equipment used in each process. The one big advantage for centrifuging and a disadvantage for creaming is that the time element is considerably longer with creaming Creaming can be accomplished in forty eight hours but to do the best job at least 20 to 25 days are required. In the long run this pays off in less freight charges and practically no after creaming. To accomplish the same result without chemical or mechanical aids would require between two and three years. Large quantities of cream are being imported that have a total solids value from 68 to 69 per cent—quite a contrast to the 61 to 62 per cent total solids of most centrifuged concentrates. About 20 per cent of the latex imported is cream.

Low ammonia cream importation was started about ten years ago. Now, about half of the cream is brought in with an ammonia content of less than 0.25 per cent. In this case, ammonia, ethylenediaminetetraacetic acid, chlorinated phenols, formaldehyde and possibly other chemicals are used as preservatives.

The general methods of creaming have not changed a great deal from those used in the early thirties. The use of small amounts of soaps[60,62], mild heat[63], agitation[64] and electric potential[65] are well worked out in practice. Some help would be obtained by reading the chapter on creaming latex of Van Gils and Kraay in Volume I of "Advances in Colloid Chemistry"[66]. High frequency currents are suggested by Leduc and Dufour[67]. An accelerated method of creaming is offered by a Netherlands patent[68] in which the main creaming tank is divided into many compartments. This idea is somewhat similar to the large number of discs used in a centrifuge and theoretically should give faster creaming. Experiments show this to be true but it also has the great disadvantage of using equipment much more difficult to clean and hence posing a greater preservative problem. However, this idea must not be completely discounted and may yet be commercially worked out.

Introduction of the soap prior to desludging[69] seems to be an excellent idea as it presents a greater opportunity for heavy metal soaps to form and to be removed, thus improving the quality of the latex. This also favors a more intimate mixing of the creaming agent with the latex, a step that always has to be carefully watched in creaming bulk quantities of latex and a factor too often overlooked.

As discussed previously in this paper the necessity of early preservation of latex before processing is important. This is just as true, if not more so, for a creaming process as it is for centrifuging. This means that the formaldehyde or similar substance used to kill bacteria should be introduced into the latex as soon after tapping as possible. This allows time for the proper addition of the creaming chemicals and protects the latex until the time when final preservatives are added. There have been cases, justifiably so, of adding some preservative in the tapping cup. However, this practice is only for special conditions. The processes suggested for reusing serum to help preserve new latex for creaming or

centrifuging should be disregarded as they only offer a small saving with the great disadvantage of lowering the quality of the concentrate.

Davey and Sekar have written two articles[70,71] on creaming agents and the theory of creaming. Both of these articles are well worth while if you are interested in this problem. The first one describes actual tests on tragacanth, konyaka meal, pectin and a few other materials. The second one discusses methyl cellulose alginate and tragacanth. Both articles offer an explanation of the mechanism of creaming and give realistic accounts as to how they believe this is accomplished.

In a nutshell, creaming is brought about by slightly decreasing the general dispersion of the rubber particles causing many individual aggregates which rise more rapidly, due to their increased size, than would the original discrete particles by themselves. These aggregating or creaming agents must effect the water balance that occurs between the particles and the suspending medium. These agents reduce the quantity of water associated with each individual rubber particle. The soap or other active dispersing agent prevents the aggregates from coalescing. The larger aggregate rises due to the difference in gravity between rubber and water. Alginate is an excellent substance to preserve the proper balance between aggregation and incipient coalescence.

C. EVAPORATION

One of the early methods of concentrating latex was by heat. Many variations were tried. Potassium hydroxide and soap has been commercially used and concentrates of over 70 per cent have been sold. Of all the early methods this seems the only one to have survived. It is still in use today. According to the literature there has been very little activity along this line. A new concentrating machine by Quasbarth[72] uses a vacuum heat concentrator for this job. The method obviously does not eliminate any of the non-rubber constituents of the latex, a fact that is generally necessary in most latex processes.

D. ELECTRODECANTATION

The use of electrical potential has been proposed by several inventors[65,73,74] in connection with chemical creaming. In these references the rate of creaming was considerably increased. Both direct and indirect current was employed. No doubt such a treatment caused some instability of the rubber dispersion and thus allowed faster rising of the rubber particles. Prior to these discoveries rubber from natural latex had been deposited at the anode by means of low voltage direct currents and formed the basis of a number of manufacturing processes.

In addition to these Pauli and Stamberger[75] brought out a method for concentrating latex by electrodecantation. They proposed to dilute freshly tapped latex to 15 per cent, preserve with about 3 per cent ammonia and put this in a three-compartment apparatus separated by diaphragms with electrodes in the two end cells. The application of a suitable direct current, reversed periodically, allowed a clear separation of the serum from the rubber. The rubber rose in the center compartment and after a few hours could be removed mechanically from the compartment at a concentration of about 60 per cent. One of the inventors, Stamberger[76], has enlarged on the practical use of this method. Further information is given by Stevens[77], Sibiriakoff[78] and by Murphy[79,80] which should be read for greater understanding of this unique method. In addition to these references Tunnicliffe[81] has written a data studded article giving

a comparison between electrodecanted and centrifuged concentrates. To those interested in details this paper should not be overlooked. It would appear that the electrodecanted product contains more rubber than is obtained by centrifuging and for that reason generally has slightly higher non-rubber constituents.

This method of concentration is being used by itself and in conjunction with centrifuging in a very practical manner by one of the larger latex producers. In a recent private communication from a representative of that company it is stated that "we have shipped many hundreds of thousands of gallons (all of bulk shipments) of electrodecanted latex and have used it in all latex manufactures in some at 100 per cent and in others as blends with centrifuged concentrate. Electrodecanted latex is a little different in its stability characteristics from centrifuged latex and for certain applications this has to be borne in mind". From the patent picture the following patents should be listed[82]. It would seem to the author that there will be a good future for electrodecanted latex.

V. ACKNOWLEDGMENTS

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CORRECTIONS

BOND STRENGTH BETWEEN TREAD AND BREAKER STOCKS

I. A. Levitan, Yu. G. Korablev, A. E. Kornev, and B. L. Babitskiĭ

An article on this subject appeared in the third issue, 1959, page 889. In the figure on p. 893 the numbering of the curves was omitted. In the figure of the original article the curves are numbered 1–5, respectively, from top to bottom at the righthand end and this numbering should be appended to the figure on p. 893 of R. C. and T.

VULCANIZATION WITH TMTD

F. M. Bevilacqua

U. S. Rubber Company Research Center, Wayne, New Jersey

There is an error in Figure 3b, p. 733, in the article, "Vulcanization with TMTD", which appeared in the July-September issue, 1959, of Rubber Chemistry and Technology. Apparently, in tracing the figure the ordinate labels were shifted. The actual values for 200% stress for the samples containing both TMTD and zinc laurate are all 50 pounds per square inch higher than is shown on the figure as published; that is, the numbers on the ordinate should be 250 and 150 instead of 200 and 100, respectively.

SULFUR GROUP ANALYSES IN NATURAL RUBBER VULCANIZATES

MERTON L. STUDEBAKER AND LESTER G. NABORS

PHILLIPS CHEMICAL COMPANY, AKRON, OHIO

In the article published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 32, page 941, it was stated on page 958:

"With the data at hand, we can calculate the relative amount of sulfur compounded in the stocks which eventually is found in the crosslinks. The data are presented in Table IV". The numerical values were inadvertently omitted from the table. The figures which should have appeared are:

TABLE IV

SULFUR GROUP ANALYSES OF CROSSLINKS

Compound No.		115	116	117	118	119	120	121	122
Cure system		TMTD "Sulfurless"		MBT +sulfur		808 +sulfur		DPG +sulfur	
Type of stock	Cure	Gum	Black	Gum	Black	Gum	Black	Gum	Black
% of sulfur compounded as S_8 (or TMTD) in crosslinks	15′	(14)	(18)	32	22	28	24	16	15
	30′	(15)	(18)	32	30	42	34	26	31
	45′	(13)	(18)	26	30	35	38	33	25
	60′	(13)	(18)	25	27	34	37	34	32
	120′	(13)	(18)	18	21	23	26	33	27

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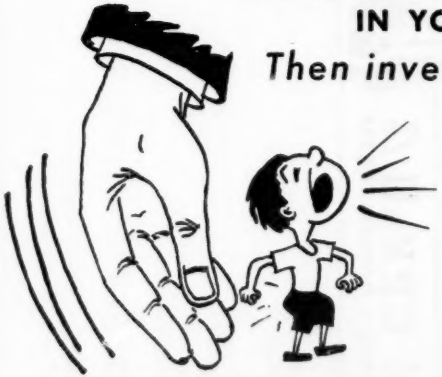

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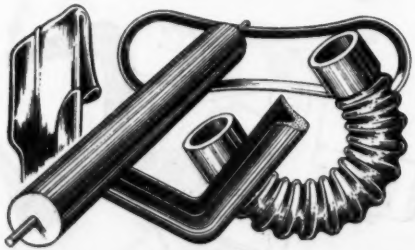

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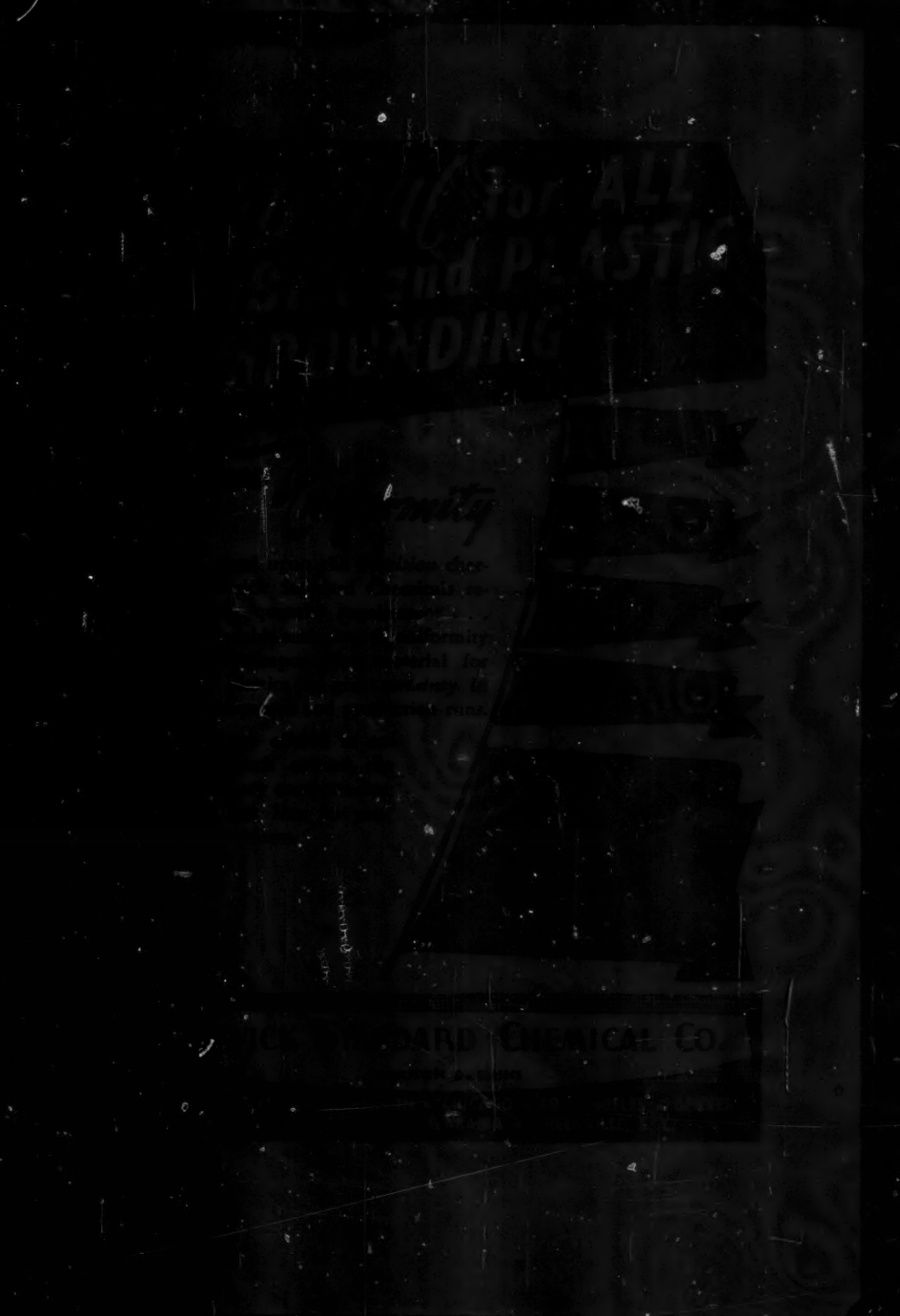
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